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**Study of the inter-annual variability of particle vertical fluxes in two moorings in the Ross Sea (Antarctica)**

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## Abstract

The most ocean - atmosphere exchanges take place in polar environments due to the low temperatures which favor the absorption processes of atmospheric gases, in particular CO<sub>2</sub>. For this reason, the alterations of biogeochemical cycles in these areas can have a strong impact on the global climate. The study of particle fluxes along the water column is therefore important to assess the transfer of the organic carbon and biogenic silica through the system. These waters have not the same efficiency in preserving organic particulate that they have for biogenic silica, so the different rate of the processes of silica dissolution and carbon oxidative degradation involves a decoupling of the biogenic silica and organic carbon cycles.

Over 20 years of Antarctic cruises (ROSSMIZE, BIOSESO 1 and 2, ROAVERRS and ABIOCLEAR projects) have led to a great archive of samples to be analyzed (cores, box-cores and sediment trap samples) in order to improve the existing biogeochemical models and to provide more accurate information on the Antarctic ecosystem changes related to global climate changes.

With the aim of contributing to the definition of the mechanisms that regulate the biogeochemical fluxes we have analyzed the particles collected in different years in two sites (mooring A and B) located in the Ross Sea in two areas with different characteristics. So it has been developed a more efficient method to prepare sediment trap samples for the analyses. This has permitted to determine the mass and biogenic fluxes and the composition of samples of a remarkable set of data. We have also processed satellite data of sea ice, chlorophyll a and diatoms concentration.

At both sites, in each year considered (1996, 1998, 1999, 2005 and 2008), there was a high seasonal and inter-annual variability of biogeochemical fluxes closely correlated with sea ice cover, which usually begins in late February and ends in mid-December. The highest values of mass and biogeochemical fluxes happened about two months after the algal bloom.

The comparison between the samples collected at mooring A and B in 2008 highlighted the main differences between these two sites. Particle fluxes at mooring A are higher than mooring B ones and they happen about a month before because mooring A is located in a polynia area with greater primary productivity and which is first sea ice free.

In the mooring B area, thanks to a consisting time series of data, it was possible to correlate the particles fluxes to the sea ice concentration anomalies and with the atmospheric changes in response to El Niño Southern Oscillations. In 1996 and 1999, years subjected to La Niña, the concentrations of sea ice in this area have been less than in 1998, year subjected to El Niño. Inverse correlation was found for 2005 and 2008.

In the mooring A area significant differences in the fluxes during two years (2005 and 2008) has been recorded. This allowed to underline the high variability of lateral advection processes and to connect them to physical forcing.

## Riassunto

Gli ambienti polari rappresentano il principale luogo in cui avvengono i maggiori scambi tra atmosfera e oceano grazie alle basse temperature che favoriscono i processi di assorbimento dei gas atmosferici, in particolare di CO<sub>2</sub>. Per questo motivo le alterazioni dei cicli biogeochimici di queste regioni, con la conseguente variazione di CO<sub>2</sub> in atmosfera, possono avere un forte impatto sul clima globale. Lo studio dei flussi di particelle lungo la colonna d'acqua è quindi importante per valutare il trasferimento del carbonio organico e della silice biogena attraverso il sistema. Non si riscontra per il particolato organico la stessa efficienza che queste acque hanno nel preservare la silice biogena, e questa differenza nei tassi dei processi chiave di dissoluzione per la silice e degradazione ossidativa per il carbonio implica un disaccoppiamento dei cicli della silice biogenica e della materia organica.

Oltre 20 anni di campagne in Antartide (progetti ROSSMIZE, BIOSO 1 e 2, ROAVERRS e ABIOCLEAR) hanno portato ad avere un enorme archivio di campioni da analizzare (carote di sedimento, *box-core* e campioni di trappole di sedimento) per migliorare i modelli biogeochimici esistenti e fornire indicazioni sempre più precise sulle variazioni dell'ecosistema antartico marino in relazione ai cambiamenti climatici globali.

Ci si è proposti quindi di contribuire alla definizione dei meccanismi che regolano attualmente i flussi biogeochimici analizzando il particolato raccolto in vari anni in due siti fissi (*mooring* A e B) situati nel Mare di Ross in due aree dalle differenti caratteristiche. A tal fine è stato messo a punto un metodo di preparazione dei campioni di trappola più efficiente che ha consentito di determinare i flussi di massa e biogenici e la composizione dei campioni di un consistente set di dati. Inoltre sono stati elaborati i dati da satellite relativi alla concentrazione dei ghiacci, di clorofilla a e di diatomee.

In ognuno degli anni esaminati (1996, 1998, 1999, 2005 e 2008), in entrambi i siti, si è osservata un'alta variabilità stagionale e interannuale dei flussi biogeochimici strettamente correlata con la copertura di ghiaccio, che di solito inizia a fine febbraio e termina a metà dicembre. I valori più alti di flussi di massa e biogeochimici sono stati registrati circa due mesi dopo i bloom algali.

Il confronto tra i campioni relativi al 2008 raccolti dai *mooring* A e B ha evidenziato le principali differenze tra i due siti. Il *mooring* A presenta flussi più alti e anticipati di circa un mese rispetto al *mooring* B perché si trova in un'area di *polynia* a maggiore produttività primaria e che si libera prima dai ghiacci stagionali.

Nella zona del *mooring* B, grazie ad una serie temporale consistente di dati, è stato possibile correlare i flussi di particelle alle fluttuazioni dei ghiacci e con le variazioni atmosferiche dovute a El Niño Southern Oscillation. Nel 1996 e 1999, anni soggetti a La Niña, le concentrazioni dei ghiacci in quest'area sono state minori mentre nel 1998, periodo soggetto a El Niño, maggiori. Correlazione inversa è stata riscontrata per il 2005 e il 2008.

Nell'area del *mooring* A le consistenti differenze registrate nei flussi relativi a due annate (2005 e 2008), hanno consentito di evidenziare l'alta variabilità dei fenomeni di avvezione laterale e di collegarli al *forcing* fisico.

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# Chapter 1

## General introduction

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### Foreword

The Antarctic region plays a key role in the global climate evolution. In the Southern Ocean it occurs the most important CO<sub>2</sub> sea-atmosphere exchange with strong carbon absorption due to biogeochemical cycles. Furthermore the differences in temperature and salinity of tropical, subtropical and antarctic waters, encountering in the Polar Front Zone, induce a high turnover of water masses and encourage exchanges between ocean and atmosphere.

In addition, in Antarctic waters it takes place 1/3 of world production of biogenic silica (Treguer and Van Bennekom, 1991). According to DeMaster (1981) about 50% of global silica due to rivers and hydrothermal emanations is deposited in the depths of the Southern Ocean.

Studies in these areas, however, are made particularly difficult by the extreme environmental conditions so it has not yet been possible to determine the role that the Southern Ocean plays in the global cycle of silica and carbon. For this reason, careful studies about primary productivity and export fluxes rates are needed.

The Ross Sea is the most productive area of Antarctica with the largest algal blooms of all the Southern Ocean (Comiso et al., 1993; Sullivan et al., 1993). It is characterized by a marked seasonal and regional variability of the primary productivity in the surface euphotic layer and in the resulting export processes along the water column. This variability is in turn linked to the processes of formation and melting of seasonal sea ice and to oceanographic processes (such as the circulation and the formation of water masses).

Mass fluxes regional variability depends both on differences in the productivity of the specific areas and on differences in currents which affect the particle sinking along the water column with lateral advection processes or particles removal. In some areas, this is considered a limiting factor for the use of sediment traps since the evaluation of vertical fluxes is much more complex (Honjo and Doherty, 1988).

The south-western area of the Ross Sea is characterized by weak currents that can carry particles of larger size not more than 20 km away. This implies that there is a good correspondence between the material produced in the area and what settles on the bottom (Jaeger et al., 1996). The north-western region is instead characterized by stronger currents that induce lateral transport even for many tens of kilometers in other environmental setting (e.g. off the shelf). The south-central part, on the other hand, shows intermediate characteristics between the previous ones (Frignani et al., 2000).

The aim of this type of studies is to understand the link between production and preservation in surface sediments in order to detect the consequences of the anthropogenic influence on carbon cycle. In fact, although the Southern Ocean is considered crucial to the global ocean processes, its role has not yet been quantitatively defined by the complexity of high seasonal variability and the cycle of sea ice formation and melting. Furthermore climate changes especially affect this area

since the ecosystem here is sensitive even to extremely small variations (e.g. a few degrees of temperature).

In this study we analyze samples from two moorings (A and B) positioned in the Ross Sea during the years 1996, 1998, 1999, 2005 and 2008 (mooring B) and 2005 and 2008 (mooring A).

The analysis of the particles collected and the study of vertical fluxes of biogenic silica, organic carbon and nitrogen allow to better determine the transport and accumulation rates of particulate matter falling to the bottom from the euphotic zone, their seasonal and inter-annual variability and their relationships with the forcing due to atmospheric phenomena such as El Niño Southern Oscillation (ENSO).

We have then processed data about sea ice extension and concentration and chlorophyll a and diatoms concentration averaged on two areas surrounding the sites, to correlate mass and biogenic fluxes to atmospheric and sea-ice conditions.

**Chapter 1** introduces the main features of the investigated area and the kind of the study. In **Chapter 2** a new method for sample treatment is proposed after a critical description of analytical methods used in literature for the determination of mass and biogenic fluxes. In **Chapter 3** it is reported a comparison between particle fluxes collected during 2008 in two sites located in different Ross Sea areas with the aim of highlighting their differences. Mooring A is located in a polynia area bordering the ice shelf in one of the areas with higher primary productivity of the Ross Sea, mooring B, instead, is positioned in the Joides basin, an area characterized by a high accumulation of bio-silica sediments and by the presence of significant processes of lateral advection. In **Chapter 4** mass and biogenic fluxes data obtained at site B during different years (1996, 1998, 1999, 2005 and 2008) are reported. The determination of a time series of data covering a period of ten years, allows a more detailed study on the inter-annual variability of biogeochemical fluxes typical of the Ross Sea. The relationships between particle fluxes and physical forcing is then investigated together with their link to the cyclic atmospheric response to ENSO variability. In **Chapter 5** the mooring A trap samples data related to 2005 and 2008 are reported and compared with the 1994 ones (Langone et al., 2003). This data underline the well known seasonal and inter-annual variability showing differences in fluxes magnitude and particulate composition. Finally in **Chapter 6** the results obtained with our research are summarized.



## 1.1 Climate

### 1.1.1 Atmospheric circulation

Antarctica is usually surrounded by a zone of low pressure, the Circumpolar Trough, the continent is instead dominated by a high pressure zone (Pidwirny, 2006).

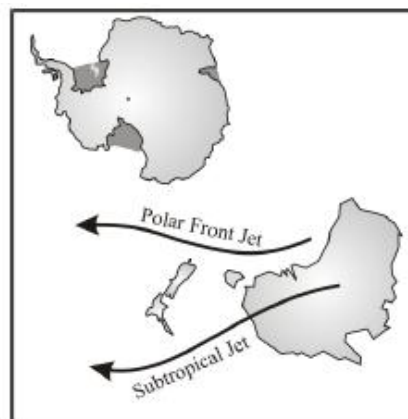
The principal atmospheric cells involved in Antarctic climate are the Subpolar Low-Pressure Cells at 60°S latitude, where the cold air masses (from higher latitude) and the warmer ones (from lower latitude) converge and the Polar High-Pressure Cells, located at 90°S, with air masses very cold and dry. Along the Subpolar Low-Pressure cells frequent storms develop causing high winds and snowfall. The Polar High-Pressure Cells are responsible of winds moving away from the Pole and forming the polar easterlies.

Between 30° to 60°S latitude, the upper air winds, flowing generally towards the pole, are deflected by the Coriolis force that causes their blowing from west to east at 60°S (Polar Jet Stream). (Pidwirny, 2006).

High vertical and horizontal temperature gradients between the continent and the nearby areas make Antarctic temperature trend particularly sensitive to changes in the low level atmospheric circulation (van den Broeke, 2000).

Some pressure systems are permanent around Antarctica and their position and strength are important for the sea ice growth and melting. One of these is the Amundsen Sea Low ( $L_{AS}$ ), a permanent low pressure zone ahead the Amundsen Sea and the Ross Sea; this low is sensible to El Niño Southern Oscillation (ENSO) so producing difference in temperature, wind strength and direction over the Ross Sea (Bertler et al., 2004).

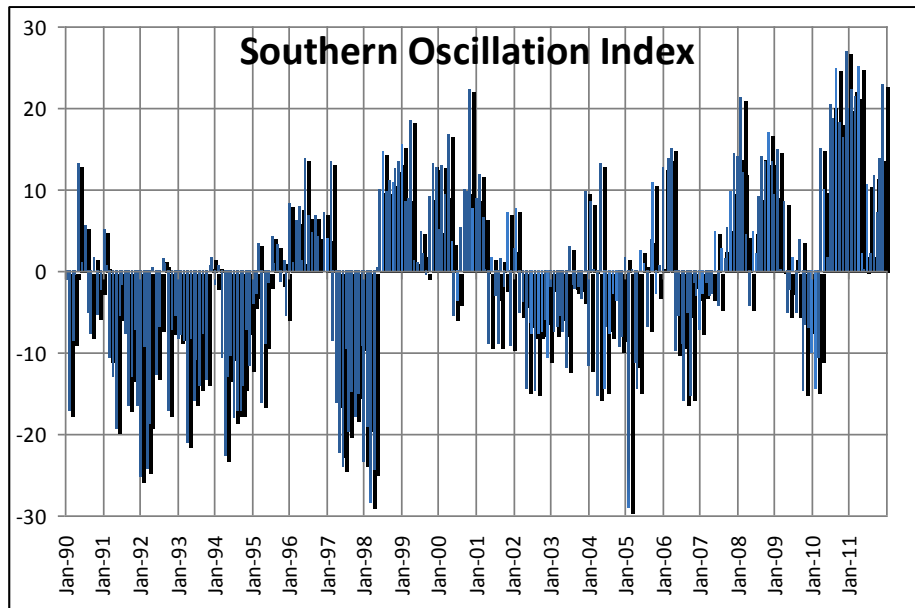
Changes in extra tropical atmospheric circulation due to ENSO forcing allow the ENSO signal transport to high latitude; some authors have attributed this connection to the stationary Rossby Wave (Karoly, 1989; Mo & Higgins, 1998; Kiladis & Mo, 1998; Garreaud & Battisti, 1999). The Rossby Wave train is one of the main circulation pattern of the Pacific and South America (PSA) pattern (Kidson, 1999).



**Figure 1:** Split jet (Polar Front Jet and Subtropical Jet) (from Bertler et al., 2006)

Another important climate feature in the South Pacific is the presence during winter of a split jet stream (Fig. 1). The jet stream flows near Australia and New Zealand and it splits into the

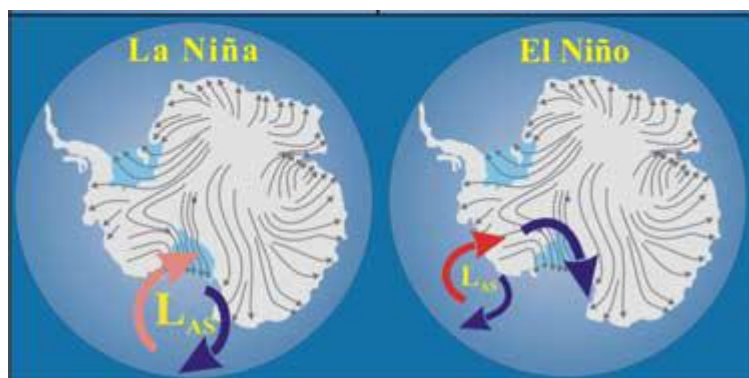
Subtropical Jet (STJ) at about 30°S and the Polar Front Jet (PFJ) at 60°S (Chen et al., 1996; Turner, 2004). ENSO cycles produce changes in the STJ and PFJ strength (Chen et al., 1996, Bals-Elsholz et al., 2001); during La Niña periods, for example, the STJ is weakened with respect to the PFJ (Chen et al., 1996; Carleton, 2003) and this makes a deeper  $L_{AS}$  which enhances katabatic winds from the continent (Bromwich et al., 1993; Chen et al., 1996; Turner, 2004).



**Figure 2:** Southern Oscillation Index annual trend from January 1990 to January 2012 (data from Bureau of Meteorology - Australian government)

In addition many other patterns have been connected to Antarctic tropospheric circulation on inter-annual or decadal scale such as Antarctic Oscillation (AAO) and Antarctic Circumpolar Wave (ACW) but the correlations between them are not well known. Strong correlations between ENSO cycles and the Ross Sea climate have been found (Kwok and Comiso, 2002; Carleton, 2003; Turner, 2004; Stammerjohn et al., 2008).

An index commonly used for ENSO is the Southern Oscillation Index (SOI), which is the normalization of differences in surface pressure between Tahiti and Darwin. Positive extremes represent La Niña periods and negative El Niño (Parker, 1983) (Fig. 2).



**Figure 3:** position of the Amundsen Sea Low ( $L_{AS}$ ) during La Niña and El Niño periods. Red arrows: warm air masses; blue arrows: cold air masses. (From Bertler et al., 2004)

The influence of ENSO on the Antarctic atmospheric circulation around the Ross Sea is mainly linked to the strength and position of the  $L_{AS}$  (Carleton, 2003; Bertler et al., 2004; Turner, 2004). During El Niño events the  $L_{AS}$  is weakened and its position changes, reaching even 1400 km eastward, with respect to La Niña periods (Chen et al., 1996; Cullather et al., 1996) (Fig. 3).

## **1.2 Southern Ocean**

The Southern Ocean is an extremely large area that constitutes about 20% of the total ocean surface. The Southern Ocean can be divided, based on the hydrographic characteristics and distribution of nutrients, in the Subtropical Convergence, the Antarctic Polar Front Zone, the Antarctic Divergence and the Marginal Ice Zone.

The Subtropical Convergence (STC), located at about 43°S latitude, is the area where warmer subtropical waters meet colder waters from higher latitudes. It shows a relatively high biomass concentration and it seems to be important for atmospheric CO<sub>2</sub> uptake, as the entire subantarctic region (JGOFS, 1992).

The Antarctic Polar Front Zone (APFZ) or Antarctic Convergence (AAC), is the wide area between the Subantarctic Front (49°S) and the Antarctic Polar Front (63°S). This area is affected by complex dynamics due to a series of current convergences. It exhibits strong gradients in temperature and dissolved silica concentration and less marked gradients in phosphates and nitrates concentrations. The Antarctic Divergence (AD) at about 65°S is the zone between the Circumpolar Current and the East Wind Drift (or Polar Current).

Finally the Marginal Ice Zone (MIZ) is the transition area between the compact ice pack and the ice free sea. This zone migrates seasonally for hundreds of kilometres and it is also subjected to inter-annual variability. The MIZ affects deep ocean areas and continental shelves, including the epicontinental margins of Ross and Weddell Seas (JGOFS, 1992).

### **1.2.1 Southern Ocean circulation**

Many currents affect the Antarctic Ocean due to the strong salinity and temperature differences between the tropical, sub tropical and antarctic ocean waters.

The presence of different water masses favours atmosphere-ocean gas exchanges and the subsequent oxygenation of deep waters.

These mixing processes mainly occur in the Antarctic Convergence (AAC) zone where the longest earth's current, flowing from west to east, develops. This current, called Antarctic Circumpolar Current (AACC), extends for about ten degrees latitude (Manzoni, 1989).

Near the Antarctic continent the Polar Current (PC) flows from East to West; its flux is influenced by the Antarctic continental winds. These two currents circulating around the continent in opposite directions are separated by the Antarctic Divergence (AAD) in which the rising of the Atlantic waters occurs (upwelling).

The Polar Front (PF) is characterized by three main water masses: the Antarctic Surface Water (AASW), the Circumpolar Deep Water (CDW) and the Antarctic Bottom Water (AABW).

The AASW is composed by surface waters forming in summer by the mixing of shelf waters and sea ice melting waters (Jacobs et al., 1985). Its temperature does not exceed 0°C and its depth reaches to the north 50-100 m.

The CDW flows below the AASW and it originates from the convergence between the North Atlantic deep current and the cold water coming from the Ross and the Weddell seas. It has a temperature higher than the AASW (1°C) and high salinity. It also represents the main source of nutrients for the coastal Antarctic waters and the main source of heat for the Ross Sea where it influences the cycle of ice formation and melting (Anderson et al., 1984).

The AABW is the water mass that flows close to the bottom of the Antarctic Ocean. It moves northward and it is formed generally by mixing of intermediate sea water with dense waters originating from the continental shelf. It consists of very dense waters and it has a temperature of about -0.4°C.

### **1.2.2 Ross Sea circulation**

In this study we focus on the Ross Sea area. The Ross Sea is an epicontinental sea bounded to the West by the Victoria Land, to the East by the Marie Bird Land and to the South by the Ross Ice Shelf and it extends for  $3.5 \times 10^6 \text{ km}^2$ .

It is characterized by a deep and steep continental shelf, a factor that significantly affects the sedimentation. One of its main peculiarities is to be counterslope, i.e. its depth increases from offshore to the coast (Frignani et al., 2003).

According to Vanney et al. (1981) the main causes of the shelf morphology are due to tectonics, whose action has been increased by volcanism and glacial erosion.

The Ross Sea morphology is also characterized by several large and deep basins which have an average depth of 500 m. This morphology is probably originated by ice tongues coming from the western ice sheet.

At the east end there is the Sulzberger Basin, deepest near the coast where it reaches 900 m depth, the central part is constituted by basins and banks with 500 m average depth and NNE direction. The west end is much steeper and formed by a succession of glaciers and volcanic islands (McMurdo Volcanic Complex), whose depth is generally greater. To the west of Cape Adare the average depth becomes 200 m and this is one of the shallower areas of the Antarctic shelf, probably because of an uplift occurred in the Quaternary.

The Ross Sea circulation is very complex and the currents distribution may have a seasonal, annual or pluriannual variability because of the close correlations between water masses, sea ice formation, sea ice melting and polynia areas. As a result of these interactions a number of water masses are formed with different temperature and salinity, they interact with each other producing layered water column. These movements significantly influence the sedimentation processes.

Furthermore the Ross Sea bottom topography has a relevant role in water masses circulation. It is in fact formed by basins and banks in which deeper areas, adjacent to the continent, saltier and denser waters converge.

From east to west the Ross Sea water column shows a general increase in salinity due to brine formation and a cyclonic circulation in the western portion of the shelf (Klepikov and Grigor'yev,

1966). According to the model of Klepikov and Grigor'yev the surface water, flow out of the Ross Sea, would be confined to a narrow strip along the coast of Victoria Land and the inflow would occupy the eastern part of the shelf (Anderson et al., 1984).

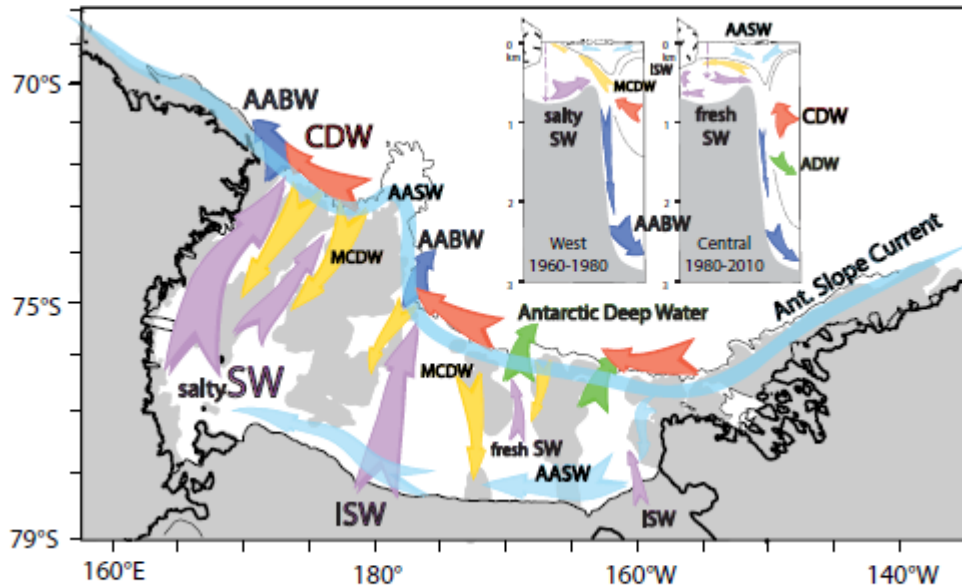
The principal water masses in the continental shelf of the Ross Sea are (Jacobs and Giulivi, 1998):

*Modified Circumpolar Deep Water (MCDW);*

*High Salinity Shelf Water (HSSW);*

*Low Salinity Shelf Water (LSSW);*

*Ice Shelf Water (ISW).*



**Figure 4:** Ross Sea circulation during the last 50 years. Antarctic Surface Water (AASW): light blue. Shelf Water (SW): purple. Modified Circumpolar Deep Water (MCDW): orange. Circumpolar Deep Water (CDW): red. New Antarctic Deep Water: green. New Antarctic Bottom Water: dark blue. (from Smith et al., 2012).

The MCDW (Fig. 4) is characterized by relatively high temperatures (between  $+1.0^{\circ}\text{C}$  and  $-1.5^{\circ}\text{C}$ ) and has its origin from the CDW which go up along the Ross Sea continental slope and blends with the cold shelf waters. This current flows between  $167^{\circ}\text{W}$  and  $177^{\circ}\text{W}$  and to the west of  $178^{\circ}\text{W}$ .

The MCDW is the main source of nutrients for the coastal waters, it allows the melting of sea ice regulating the Ross Sea circulation (Anderson et al., 1984).

The HSSW, that probably forms during winter in the Terra Nova Bay polynia, flows in the southwestern Ross Sea, it has a salinity of  $34.8\text{‰}$  and a temperature close to the freezing point (about  $-2^{\circ}\text{C}$ ). This is the main current of this sector during summer.

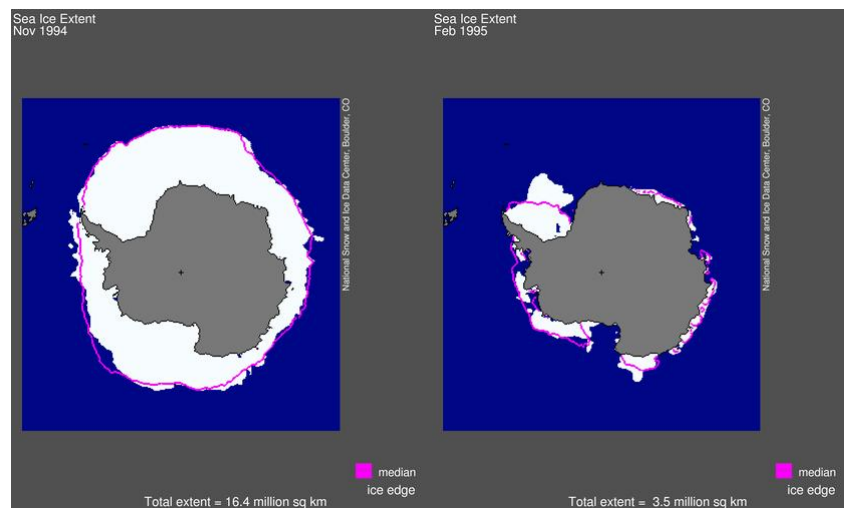
The LSSW flows in the eastern Ross Sea, where ice cover is permanent. These waters are formed by the melting process that occurs at the beginning of the austral summer and that releases waters at lower salinity. The LSSW, in fact, has a salinity of  $34.5\text{‰}$  and a temperature of about  $-1.5^{\circ}\text{C}$ . So when the LSSW meets the HSSW the first flows above the other because of its lower density.

The ISW (Fig. 4) is formed by waters having temperatures below the freezing point of the sea surface ( $-2^{\circ}\text{C}$ ). In fact, these waters are cooled by the interaction with the ice shelf base and they flow between  $177^{\circ}$  and  $179^{\circ}\text{W}$  at a depth of 500 m with a NNE direction starting from the ice shelf. Near the continental slope some of these waters form the AABW.

### 1.2.3 Sea ice

The sea ice begins to form around the coast from February to March, it reaches its maximum extent (26 million km<sup>2</sup>) on September, at the end of the Austral winter (Fig. 5). This process is very quick and begins when the top of the water column, which has a height of approximately 30-40 m, reaches a temperature of approximately -1.8°C, i.e. the freezing temperature. The ice layer covering the sea has a thickness of 2-3 meters, it extends with a speed of about 4 km per day and reaches a surface twice the continent. The sea ice around Antarctica every winter has an extension of 1,300 km and so it isolates the mainland by all the other continents.

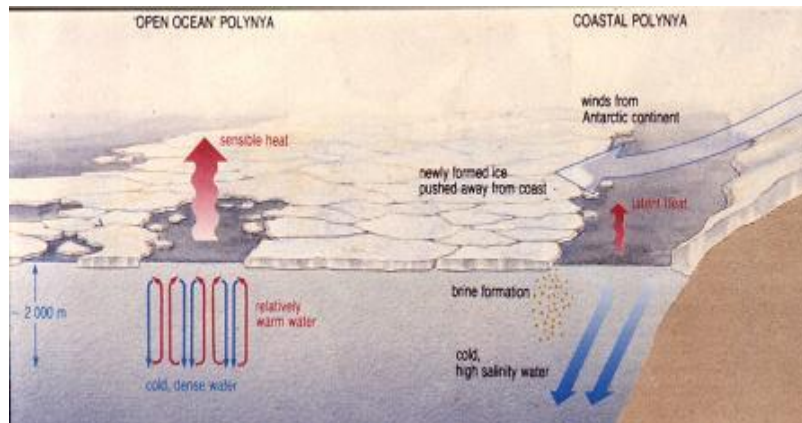
During spring, with the ice melting, the ice-sheets move away from the ice pack with a speed that can reach up to 65 km per day.



**Figure 5:** sea ice extension during (a) November and (b) February (from EOS Distributed Active Archive Center)

The ice cover is not a continuous stretch, in fact there are ice-free zones, ranging in size from 1 to 10 km, called channels. In addition to the channels there are large areas, called polynia, that may have an extension of up to 350,000 km<sup>2</sup> and that are ice free throughout the year (Gordon and Comiso, 1988).

There are two main types of polynia: the coastal and the open ocean (Fig. 6). The coastal polynia develops when the katabatic winds, which blow from the Antarctic continent, push the new formed ice offshore creating a ice-free zone between the coast and the pack. The extension of this type of polynia can be up to 100 km. The katabatic winds form on icy highlands due to the gravity currents generated by the strong cooling that takes place on the continent, these winds reach the coast following the glacial valleys (Gordon and Comiso, 1988).



**Figure 6:** coastal and open ocean polynia formation (from [www.mna.it](http://www.mna.it))

The mechanisms that originate the open sea polynia, instead, are still not at all clear, although some hypotheses have been put forward. The most accredited by various authors is that the open sea polynia is being generated for the onset of convective cells, i.e. for the settling of a vertical movement mechanism. The Circumpolar Deep Water, a relatively warm water, raises to the sea surface because it is less dense, but here it cools, sinks again and it is replaced by other "warm" water, which in turn reaches the surface, thus generating convective cells. This type of convective cells may be formed in many ways, but only some of these give rise to a polynia; this occurs because of the intensity of the process. In fact, if the "warm" water that goes up melts part of the ice, it forms a layer of fresh water that, being less dense than sea water, remains stable on the surface and thus prevents the hotter water to reach again the ice layer and melt it. If the fresh water layer is not sufficient to stop the convection, more ice can flow in the area increasing the layer of fresh water and thus stopping the process.

The polynia may be able to self-renew if it reaches a surface large enough; in fact, the area where the convection occurs is proportional to the square of its radius and the amount of ice that can flow in polynia is proportional to the perimeter; if a polynia has a radius greater than a certain minimum value the ice can flow rapidly enough to stop the convection and hence the polynia does not die.

The open ocean polynia could have a significant effect on the climate because a surface free of ice releases heat to the atmosphere more rapidly. It is not known, however, if the frequency of polynia formation is sufficient to cause such effects (Gordon and Comiso, 1988). In addition, free water can exchange gases with the atmosphere much more readily than the layer of ice and this could affect the chemistry of the ocean and the atmosphere, altering the normal atmosphere-ocean interaction and thereby generating consequences on climatic conditions on a global scale.

It has also been noted that when polynia areas expand there is an increase of primary productivity in both ice-free areas and in those with ice cover (Gordon and Comiso, 1988; Tremblay and Smith, 2007).



### 1.3 Biogeochemical cycles

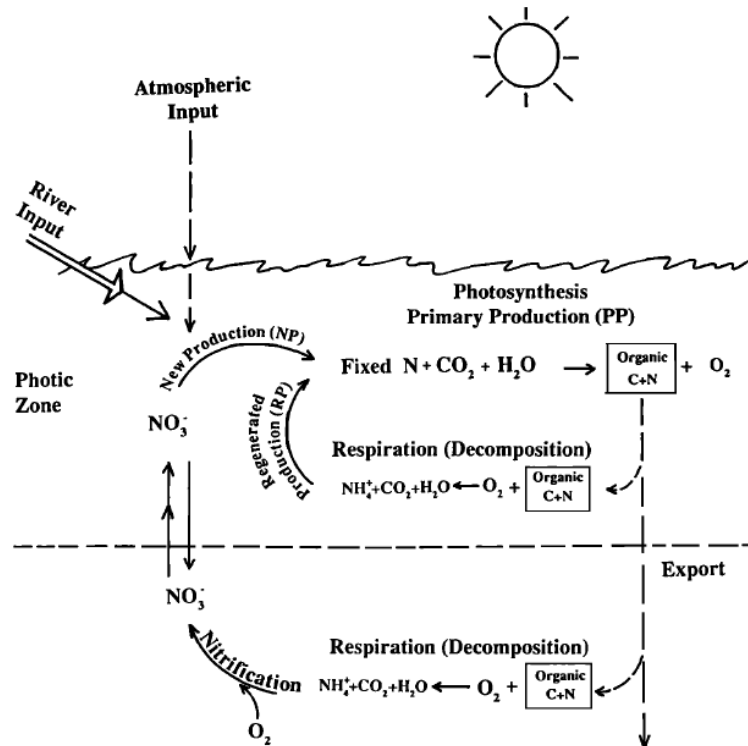
The biogeochemical cycles are the path followed by a chemical element within the biosphere.

Biogeochemical cycles play an important role in sequestering CO<sub>2</sub> from surface waters and in its transport to the seafloor. Diatoms, in all the oceans, constitute an important component of the biological pump. In the Southern Ocean, in particular, diatoms are the main source of organic material exported as underlined by the same temporal pattern of the carbon and silica fluxes. In these waters, however, there is a decoupling of carbon and silica cycles greater than at any other latitude, resulting in high rates of silica accumulation and sediments poor in carbon (DeMaster et al., 1992; DeMaster et al., 1996; Nelson et al., 1996).

#### 1.3.1 Primary productivity

The primary productivity is defined by the conversion rate of dissolved inorganic carbon and nutrients in organic matter through the photosynthesis (Jahnke, 1990). In the surface layer most part of biogenic material is recycled by oxidation, decomposition or predation. Then only a fraction settles to the bottom.

Primary production can be divided in new production (NP) and regenerated production (RP). The first is due to nutrients supply through rivers and atmospheric inputs or upwelling. The second is due to nutrients recycled in the euphotic zone (Jahnke, 1990) (Fig. 7).



**Figure 7:** schematic representation of carbon and nitrogen cycles in the surface layer of the water column (from Jahnke, 1990)



The average primary productivity in the Southern Ocean has been estimated to be under 40 gC/(m<sup>2</sup>yr) less than 5% of the global one. It is estimated that at the Southern Ocean seabed occurs only 11% of total organic carbon accumulation but about 50% of bio-silica accumulation (DeMaster, 1981; DeMaster et al., 1992; Smith and Nelson, 1986; Nelson et al., 1996).

There are two possible causes for this fact: higher bio-silica production or higher bio-silica preservation.

The biogenic sediments accumulation is related to the primary productivity of the photic zone, and in particular, at high latitudes, to the production of bio-silica. The primary productivity is influenced by many physical and chemical parameters such as: temperature, irradiation, ice cover and the amount of nutrients available in the water.

- Temperature: it affects the primary productivity and it especially affects the dissolution of some elements sinking to the bottom. Low temperatures raise the Carbonates Compensation Depth (CCD), causing in the Southern Ocean a greater dissolution of carbonates.
- Irradiation: it is essential for photosynthesis and it controls the growth of phytoplankton at seasonal and daily scale. The ice extension strongly reduces irradiation so inhibiting the photosynthesis.
- Ice cover: during periods of maximum expansion of ice there is a reduced growth of microorganisms which can however be trapped alive in the ice and, thanks to ice porosity that allows them to interact with the sea water, proliferate. When seasonal sea ice melts the higher temperature, the water column stratification and the availability of nutrients create the conditions for the development of algal blooms.
- Nutrients: the primary productivity is also influenced by the amount and type of nutrients dissolved in water. The main ones are C, N, Si and Ba. Fe also has a key role in photosynthesis, because it acts as a catalyst, and its influence is currently under study.

The Ross Sea primary productivity shows a high temporal and regional variability: the first due primarily to the expansion and retreat of sea ice, the second to the presence of different groups of organisms.

The productivity is negligible from mid April to early September, during the period in which there is no direct light, while the maximum productivity occurs between mid-September and early November. The retreat of ice occurs in early austral summer first in the polynia areas and then northward. So algal blooms occur first in the south-west and south regions and then it extends to the northern one. This causes two main positive gradients in primary productivity: from north to south and from east to west. Algal blooms occur mainly in ice edge areas during the sea ice retreat, this is because the colder and fresher water released from the ice, adds to the nutrients brought to the surface from deep water (upwelling) and creates the favorable conditions to algal development.

Primary productivity in the Ross Sea shows regional differences: diatoms dominate the northern, the south-western and the south-eastern regions while the south-central area of the basin is dominated by not siliceous algae (*Phaeocystis antarctica*) (Smith et al., 1996). In particular the south-western area is characterized by the highest rates of sediment accumulation and by surface sediments with the most biogenic silica content and the northern area shows the lower productivity of the Ross shelf due to the greater persistence of ice compared to other sectors.

In the Ross Sea primary productivity is relatively high if compared to the rest of the Southern Ocean, although it does not reach the levels of low latitudes shelves. Nelson et al. (1996) have estimated an annual primary productivity in the Ross Sea of about 91 gC/(m<sup>2</sup>yr) in the northern region and 216 gC/(m<sup>2</sup>yr) in the southern one with an average value of 142 gC/(m<sup>2</sup>yr) on the entire sea.

### 1.3.2 Particle fluxes

Particle fluxes in the Ross Sea depend mainly on the primary productivity that occurs in the first 100 m of the water column. The amount and the type of material that subsequently falls along the water column (passive flux) depend on the development of phytoplankton and on the different associations of organisms. Aggregates and fecal pellets produced by zooplankton, which are mainly present in the south-west area and decrease with depth, are an important part of the passive flux (Nelson et al., 1996). The predominant algae in the Ross Sea are diatoms (in the south and north-west) and *Phaeocystis antarctica* (in the east). Usually diatoms undergo the grazing by zooplankton and belong to the passive flux simply sinking to the bottom or like fecal pellets. The *Phaeocystis Antarctica*, instead, is less easily preyed and then it contributes to the passive flux mainly like aggregates (Smith et al., 2003).

Previous investigations (Langone et al., 1996; Langone et al., 2000) performed in mooring A and B sites documented at both sites an high seasonal variability and similar trends of carbon and silica fluxes denoting a common source (diatoms) for both elements (Nelson et al., 1996).

In site A (Langone et al., 1996) the mass and biogenic fluxes have their peak between March and April, with a delay compared to the highest levels of primary productivity of about two months and they show, along the water column, organic carbon degradation four times greater than bio-silica dissolution.

At mooring B (Langone et al., 2000) lateral advection and resuspension processes have been documented with an amount of sediment collected at the bottom an order of magnitude greater than the one collected at the top.

### 1.3.3 Carbon cycle

In polar environments occur the greatest exchanges between atmosphere and ocean due to the low temperatures that favour the atmospheric gases absorption processes. In particular, the Southern Ocean accounts for 20-25% of the annual oceanic uptake of CO<sub>2</sub> (Takahashi et al., 2002). For this reason the alterations of biogeochemical cycles in this region may change the percentage of CO<sub>2</sub> in the atmosphere and have a potential impact on the global climate. In addition, changes in the environment arising from the modern increase in atmospheric CO<sub>2</sub> content are expected to produce changes in the sea ice extent and stratification in the water upper column, changes that can profoundly affect the carbon cycle in these regions (Sarmiento et al., 1998). Although the Southern Ocean presents some areas of high productivity, its contribution to the oceanic carbon cycle has not

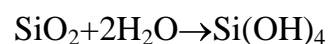
yet been well quantified also due to the high regional and temporal variability, whose causes have to be better defined.

The carbon export processes from the surface depend on the algal bloom, on the vertical fluxes of particles and on the sedimentation rates. All these processes are related not only to the intensity of the algal bloom but also to the characteristics of the dominant species of phytoplankton which in turn influence the food-web. Phytoplankton with different sizes and aggregation forms have different characteristics of vertical speed, drop and biodegradability.

In the Ross Sea, phytoplankton assemblages consist mostly of colonies of diatoms and *Phaeocystis antarctica*. The bloom formed by these organisms has high rates of CO<sub>2</sub> export fixed autotrophically in the surface mixed layer, but they differ substantially in their contribution to the biogeochemical cycle (Arrigo et al., 1999). Diatoms are in fact subjected to grazing, resist to surface microbial degradation and fall into aggregates or like fecal pellets because of digestive processes. Colonies of *P. antarctica* are little subjected to grazing by mesozooplankton and microzooplankton and once aged they are subjected to different fates depending on the physical and chemical characteristics of the environment. They can be exported during periods of rapid growth or precipitate after the maximum bloom or yet they can be lysed in the surface layer and remineralized giving rise to negligible sediments. The phytoplankton represents a habitat extremely rich in bacteria that contribute to the remineralization and enzymatic dissolution of the particulate organic material both at the surface and during the sinking. Their activities may affect the biological pump (Becquevort and Smith, 2001).

#### 1.3.4 Silica cycle

The greater part of the siliceous sediment at the bottom is due to the primary production. In the surface water the bio-silica is fixed in the skeletons of diatoms and other organisms, and, at the death of such organisms, partly it dissolves in water, forming silicic acid according to the reaction:



This process occurs during the sinking of dead organisms, mostly in the first 100 meters (euphotic zone), involving 50% of silica produced by diatoms.

In the deepest layers, silica is instead attacked by bacteria and partly recycled; the remaining silica settle down to the bottom, but this is a small fraction of the silica produced in the euphotic layer. The dissolution process continues in the bottom waters and in the first few centimeters of sediment. The factors that affect the preservation of biogenic silica are:

- sinking speed: faster is the fall and lower is the dissolution in the first 100 m;
- cells thickness and size: it can make difficult for bacteria to attack the organisms;
- water concentration of Si(OH)<sub>4</sub>;
- temperature: high temperature favor the dissolution of silica, which is why in the Antarctic areas, as the Ross Sea shelf, there is a high accumulation rate of bio-silica (Kamatani, 1982).

In the Antarctic region is stored about 75% of the modern accumulation of biogenic silica in marine sediments. Such high accumulation rate was initially attributed to high primary production due to increased availability of nutrients in Antarctic waters. Direct measurements have shown that this production is rather moderate, so the massive accumulation of silica is due to the environmental conditions that allow an excellent preservation of biogenic silica (Langone et al., 1998).

The accumulation of silica is due to organisms that fix this element in their skeleton, so the distribution of silica in the sediments depends on the areas of primary productivity and on the seasonal variability of this production, which in turn depends on sea ice and sea currents.

## 1.4 Moorings

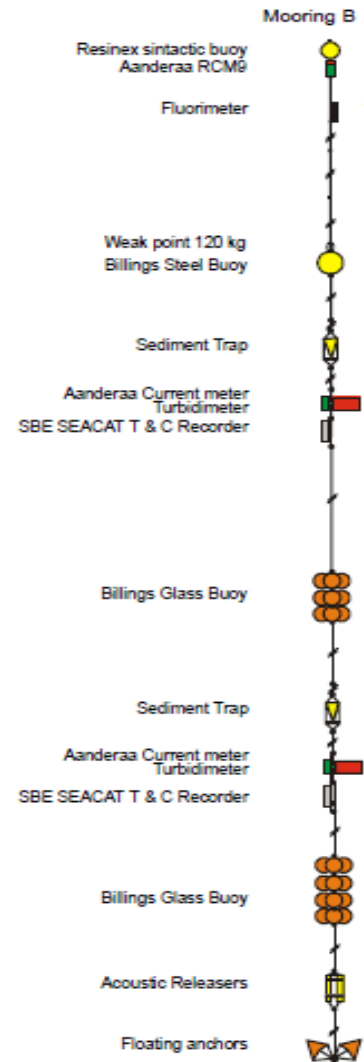
One of the main systems for the data collection such as temperature, salinity, current speed and for the analysis of particles fluxes along the water column is constituted by moorings.

A mooring is an instrumental chain that is submerged in the sea and held vertically by a series of buoys. Usually the top part is located at about 200 m depth in order to avoid damage due to sea ice while the lower part is fixed to the bottom using an anchorage. The chain may consist of multiple levels of instruments, everyone usually consisting of a CTD, a current meter and a sediment trap in order to record the characteristics of the water column at various depths. These instruments usually record data for one or two years, as long as the mooring is left in the sea, and therefore they allow to obtain continuous time series of data with measurements made even every half-hour. In Figure 8 it is shown the structure of mooring B positioned during an antarctic cruise. The mooring was composed of two current meters, two Sea Cat, two sediment traps and acoustic releasers.

Vertical fluxes along the water column are determined through the collection in the sediment traps of the particulate matter falling from the euphotic zone.

### 1.4.1 Sediment traps

Sediment traps are formed by a collection system, cone-shaped or cylindrical, whose bottom is connected to a bottle that has the function of containing the material sinking. For a long term sampling it is used an automatic system which, at fixed intervals, rotates a circular support on which the bottles for the sample collection are placed.



**Figure 8:** an example of mooring composition

Sediment traps capture the particles principally thanks to the water pressure reduction due to the Bernoulli law: an increasing in speed caused by throttling the flux which enters into the trap due to a lowering of pressure.

The low pressure inside the trap causes a water and then a particles backwash. The analysis of the material collected into the traps allows to determine the nature of the particles and the estimation of the vertical fluxes in the water column. Particles collected in a sediment trap are of two types: those who enter by gravitational fall, as fecal pellets or empty shells, and which have therefore to be considered as passive flux, and the organisms that enter into the trap swimming (called "swimmers"). To a correct fluxes evaluation it is necessary to distinguish passive from active fluxes. So all the organisms that enter "voluntarily" in the trap swimming have to be removed from the sample to avoid an overestimation of fluxes. These organisms may be, for example, protozoa of small dimensions, as flagellates and ciliates, or of larger sizes as foraminifera and radiolarians, pteropods and small arthropods.

The swimmers, furthermore, once inside the trap can feed the collected material and thereby cause a particle loss, for this reason it is necessary to use preservatives poisons inside the bottles.

Usually along a mooring are positioned some sediment traps, this allows to determine how the sinking material is modified during the fall, for example due to degradation processes.

Many studies have been carried out on the efficiency of sediment traps. From this point of view the cylindrical traps are better, but for long term sampling and in areas with low sediment fluxes, as the Southern Ocean, conical traps are considered more efficient because they have a large collection surface (GOFS, 1989).

Sediment traps are also useful to have information about the recent sedimentation. By comparing the sediment traps results with the ones related to older sediments at the sea floor, it is possible to better interpret the climate changes that have occurred in the past and to predict future changes

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## Chapter 2\*

### A revised sediment trap split procedure

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#### 2.1 Abstract

We propose a method for the treatment of sediment trap samples, with the aim of combining precision and practicality. First we review the different methods for sample processing described in the literature. The most important differences are related to the mesh size used for removing “large” particles or aggregates (from 150 micron to 1 mm), the use (or not) of filters, and of a microscope for picking out “swimmers”. The procedure presented here combines methods used at ISMAR – CNR Bologna and at Stanford University. We recommend the removal of all the organisms entering the trap alive (swimmers) using a 650 micron mesh, analysis using a stereomicroscope, and quantitative subdividing using a Peristaltic Pump.

#### 2.2 Introduction

Particle fluxes represent an important measure for evaluating the transfer of organic carbon and biogenic silica through the water column. The conversion of dissolved CO<sub>2</sub> to biological materials followed by particle export lies at the heart of the biological pump. Understanding the role of particle fluxes is therefore crucial for evaluating C exchange between atmosphere and ocean. Biogenic material accumulating on the sea floor is controlled by the balance between export of particulate matter from surface waters and losses that occurs during as material sinks through the water column.

Due to photosynthetic processes carbon dioxide is fixed by phytoplankton and then transferred to deep waters below the mixed layer mainly through gravitative particulate settling, physical mixing or zooplankton vertical migration.

Particulate export dynamics depend on the relationship between particle supply, production, consumption and aggregation and so they are controlled by biological and physical factors. Particulate export is subjected to seasonal and inter-annual variability as well as to short-term climatic events (Buesseler et al., 2007).

Nutrient availability controls phytoplankton growth processes which are the main source of particulate organic carbon in the water column.

Marine biogeochemical cycles play a key role in controlling atmospheric CO<sub>2</sub>. About 20 to 25% of the annual CO<sub>2</sub> oceanic uptake occurs in the Southern Ocean (Takahashi et al., 2002), so the biogeochemical changes that affect this region may influence atmospheric pCO<sub>2</sub> levels and have an important impact on global climate.

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To predict future changes in the level of atmospheric CO<sub>2</sub> and to interpret changes that happened in the past it is necessary to determine ocean carbon export rates on a global scale as well as the factors that can alter the carbon cycle.

Sediment traps are one of the more important tools used to collect quantitative information about particulate matter falling from the euphotic zone toward the seabed. Sediment trap data sets are used to determine temporal variability in particle fluxes and to investigate the mechanisms that regulate biogeochemical fluxes in the oceans.

The analysis of materials collected by sediment traps determines the composition of the particles allowing an estimation of a variety of vertical fluxes (e.g. organic C, radiolarians, biogenic silica, calcium carbonate) through the water column as well as their seasonal variability. The export of POC, produced by phytoplankton in the euphotic layer, gives an estimation of the efficiency of the biological pump (Ducklow et al., 2001).

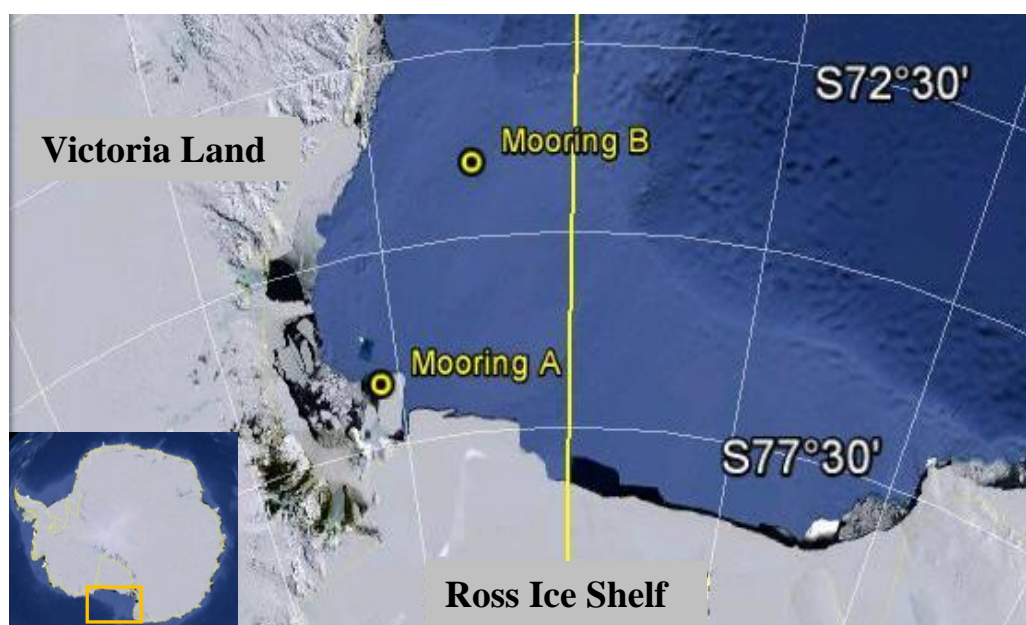
In order to study samples from sediment traps a series of procedures are generally followed.

The particles collected by sediment traps are generally composed of a mixture of biogenic materials and lithogenic components (Deuser et al., 1981; Jickells et al., 1984) as well as occasional and typically minor pollutant phases (Jickells et al., 1984; Knap et al., 1986).

Regarding the biogenic components, it is first necessary to discriminate between passive and active flux in the water column. The material collected in a sediment trap can be divided in two groups: dead organisms that entered the trap via gravitative settling (sinkers), fecal pellets, empty shells or algae (passive flux), and live organisms that actively enter the trap (swimmers). The aim of particles flux studies is to assess the export rate of the biogenic component from the surface layers, so only the passive flux must be considered and swimmers have to be identified and then carefully removed.

Additional problems include sample preservation, the instruments used for the splitting, the mesh size of any sieves used and the methods of dispersion of material during the operations.

The aim of this paper is to propose a methodology to process samples collected by sediment trap in order to optimize the accuracy and time-efficiency of the procedures used at ISMAR-CNR-Bologna (Heussner et al., 1990) to process Antarctic sediment trap samples. The accuracy in the procedure for the treatment of sediment trap samples is crucial for two reasons: these areas are difficult to reach and, at the same time, their investigation allows to understand the biogeochemical processes at global scale. Thanks to various research projects (ROSS-MIZE, BIOSO I and II, ABIOCLEAR, ROAVERRS and VECTOR- FISR-Minister of University and Research), coordinated by Institute of Marine Sciences - National Research Council - Bologna, two moorings (A and B) were deployed in two different areas of the Ross Sea (Fig. 1) since 1991 and the material has been collected during several oceanographic cruises from 1991 to 2010.



**Fig. 1.** Moorings A and B location in the Ross Sea (Antarctica)

## 2.3 Review of procedures from the published literature

There is no single, standardized sample processing methodology in use today.

Depending on the composition and origin of the collected samples different protocols are adopted. For example, in samples with large swimmers a larger sieve may be used for removal relative to samples where the organisms are smaller.

The various methods differ principally in whether swimmer removal is accomplished by picking or sieving, as well as the specific methods of splitting and drying (Table 1).

The use of a different splitter modifies the precision of the measurement of the sample mass, whereas a different method of swimmer removal may affect the biogenic fluxes values.

Some authors (Conte et al., 2001; Honjo and Manganini, 1993; Miquel et al., 1994 and Karl et al., 1996) use one or more sieves with different meshes (125, 500, 600, 1000, 1500 micron and 1 mm) before splitting to remove the larger swimmers or flocculent materials. This procedure is followed, sometimes, by swimmer picking under a microscope with different magnifications (Miquel et al., 1994 and Conte et al., 2001). In some cases swimmer removal is done only with sieving (Honjo e Manganini, 1993 and Karl et al., 1996).

Others (Steinberg et al., 2001 and Antia et al., 1999) remove swimmers only by picking under microscope.

Splitting and drying methods vary widely with respect to the different analyses to be performed. In Table 1 we report these methods and in some cases the devices used.

Some authors (Steinberg et al., 2001; Antia et al., 1999 and Karl et al., 1996) split the entire sample into 4 fractions (Karl et al., 1996) or in a range between 1/8-1/128 splits (Antia et al. 1999); others use different splitting schemes depending on the particle size (Conte et al., 2001; Honjo and Manganini, 1993 and Miquel et al., 1994).

**Table 1**

Different splitting methods (from Buesseler et al. 2007 modified). \*See geographical details in reference.

Investigated area*	Trap depth	Time for picking	Mesh size (if used)	Type of picking	Splitting method	Reference
Bermuda Atlantic Time-series Study (BATS)	150 200 300	1-2 hours	none	with 250X and 500X magnification	VERTEX method	Steinberg et al. 2001
Hawaii Ocean Time-series (HOT)	800 1500 2800 4000	0 hour	1000 micron	None	Sample splitted in 4 fractions with a rotating splitter device	Karl et al. 1996
Mediterranean Sea	80 200 1000	0.5-1 hour	1500 micron and 600 micron	In solution and with 50X magnification	After sieving through 1500 micron sieve, 1/4 or 1/8 of the liquid sample is put apart. The remain sample, after sieving and picking, is desalted and freeze-dried	Miquel et al. 1994
European continental margin	600 and 1050 at a site 600, 1440 and 3220 at the other site	About 3-5 hours 9 if there is a high flux	none	120X	Samples splitted in a range between 1/8 and 1/128	Antia et al. 1999
North Atlantic Bloom Experiment (NABE)	1000 2000 4500 or 3500	0 hour	1000 micron	None	>1000 micron fraction splitted in 4 subsamples; <1000 micron splitted in 4 and then in 10 to obtain 40 subsamples. Device: rotating wet sediment splitter	Honjo e Manganini 1993
BATS (Ocean Flux Program, OFP)	500 1500 3200	0-2 hours	1000 micron, 500 micron and 125 micron	Only for >500 micron fraction with 50X magnification	>1000 micron: oven dried at 50°C <1000 micron: splitted into 10 subsamples. Device: McLane rotary splitter	Conte et al. 2001

Conte et al. (2001), in order to use the sample for organic geochemical analyses and reduce the potential trace metal contamination, split the sample with 1000 and 500 micron meshes and subsequently remove swimmers by picking. Then they oven dry the >1000 micron fraction at 50°C, recombine the <1000 micron fractions and split it into 10 subsamples. Three or four of these subsamples are set aside for analyses, the remaining subsamples are recombined and sieved with

500 and 125 micron meshes. The sieved fraction are oven dried and the <125 micron fraction is centrifuged and freeze-dried.

Honjo and Manganini (1993) use only one sieve with 1000 micron mesh size. They split the >1000 micron fraction into 4 parts with a rotating wet sediment splitter. The <1000 micron fraction is split first into 4 parts and then each of these subsamples is further split into 10 parts so they obtain a total of 40 subsamples.

We have derived the modified method described below from the methods in use at Stanford University and the Heussner procedure in use at ISMAR - CNR Bologna that we describe in detail in the next paragraphs. We have chosen these two methods because they are both used to process Antarctic sediment trap samples.

### 2.3.1 Stanford University method (R. Dunbar and D.A. Mucciarone).

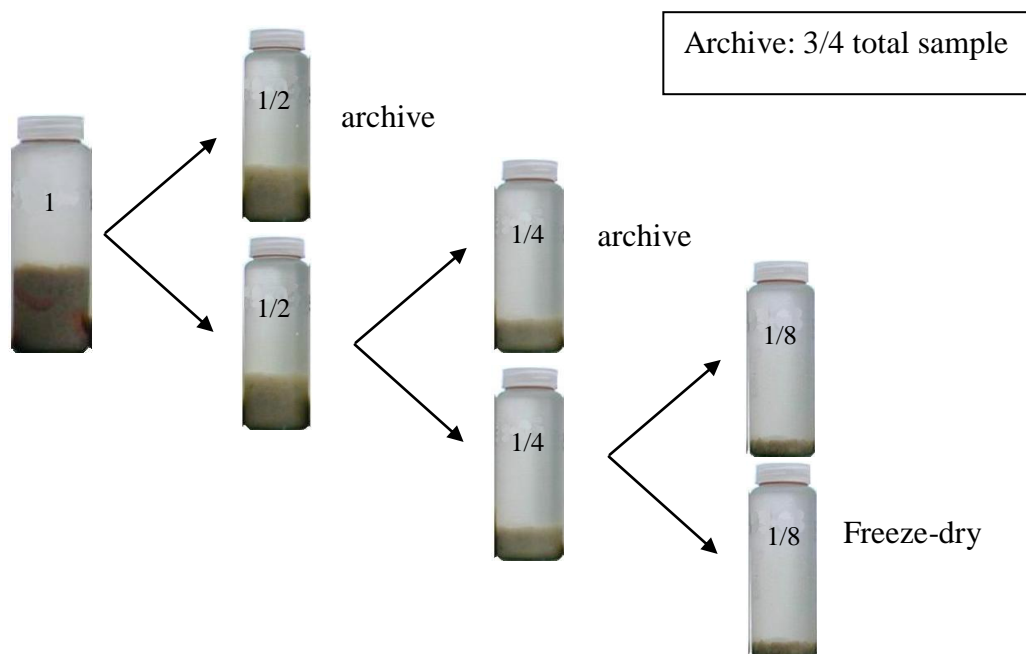
This method use a Folsom Plankton splitter (McEwen et al., 1954) instead of a Peristaltic Pump to split the sample. The splitter consist of a wheel divided into two parts; this wheel is rotated back and forth several times to divide the sample into two halves.

The sample's supernatant is taken and inserted into a squirt bottle (150 ml). This is used to clean the splitter and all the containers from particles in order to fully recover the split sample material.

This process is repeated on successive subsplits, depending on the amount of the sample available and the numbers and sizes of subsamples desired (Fig. 2).

Before the two fractions obtained are put in their respective containers picking is performed. Samples are placed into two trays and every organism recognized as a swimmer is taken out using forceps with the aid of a magnifying glass or dissecting microscope (depending on the swimmers size). The organisms considered as swimmers are those that are quite fresh in appearance because, usually, zooplankton that dies and falls into the trap sample shows some loss of integrity.

Swimmers are placed on a pre-weighed filter and are oven-dried before being re-weighed and analyzed (species, size classes, etc.).



After this procedure two fractions of the sample and a recombined portion that will be preserved as an archive are obtained. One of the two fractions is placed in a bottle and preserved wet while the second is placed in a test tube and subjected to a freeze-drying treatment that follows:

- Place the 50 ml tube in the centrifuge,
- Centrifuge for 10 minutes at high speed to settle the entire sample at the tube bottom,
- Remove salts by adding DeI water and resuspend the sample prior to a second centrifuge,
- Let it sit and further settle for a few days,
- Pipette off the supernatant liquid from the tube being careful not to remove sediment,
- Remove as much supernatant as possible,
- Close the tube with perforated parafilm,
- Place the tube in a freeze dryer until it is dry.

### *2.3.2 Heussner method – ISMAR CNR Bologna (Heussner et al., 1990)*

This method begins with the removal of swimmers. The coarse fraction is separated from the fine fraction with a 580 µm nylon mesh (with the aim of making the removal of swimmers easier). All swimmers are removed from both fractions using forceps and a stereomicroscope. The organisms collected are preserved in formalin for further analysis.

After swimmer removal the sample is split as follow: a splitting scheme that depends on the amount of the sample, on the analyses to be performed, and on the amount of sample required for each analysis is set up. Additional provisions are made for regular replicate analyses.

The sample is put into a 2l glass flask and it is split using an orbital shaker to obtain a suspension as homogeneous as it is possible, and a precision peristaltic pump connected to a mechanical arm collects sample aliquots of fixed volume and delivers them to different subsample beakers. Then one or more of these subsamples are chosen and the same procedure is repeated until the planned number and sizes of subsamples are obtained.

During this operation, the sample is diluted several times with sea water from the sampling region. After this the next step is filtering.

Filtering is performed on the sub-samples provided for the analysis that need dry sediment, such as biogenic silica, metals, and carbon analysis.

There are many types of filters (e.g., Nucleopore (polycarbonate), Millipore (cellulose)) available for use depending on the analysis to be performed.

## **2.4 Discussion**

These last two methods are well tested and compatible, they have been used on Antarctic sediment trap samples showing comparable results (Langone et al., 2003; Dunbar et al., 1998). For these reasons we thought to modify the Heussner method by replacing some steps with those adopted at the Stanford University.

The main difference between the two methods lies in the way the sample is arranged for the analysis. The Heussner method involves the use of filters for acquiring dry material, while with the USA method we obtain a sample fraction via freeze drying. The main advantage of using the U.S. splitting method lies in not having to pre-treat samples. The pre-treatment, necessary to remove the organic component and the carbonatic fraction, implies more steps and, consequently, a longer time and a possible increase of the error.

In addition, the choice of removal of swimmers only from subsamples that will be subsequently analyzed offer potential time savings.

The U.S. method also foregoes a time-consuming preliminary planning stage, which consists of deciding the most appropriate split according to the mass of sample and the type of analyses desired.

Having a single fraction of a dried sample allows us greater flexibility with respect to which analyses to perform and we are not compelled by the initial choice but we can repeat an analysis several times if necessary. Positive and negative aspects are illustrated in Table 2.

#### *2.4.1 Picking*

Failure to remove swimmers may result in an overestimate of the passive sediment flux. Swimmers are defined as any living organism that enters the trap alive, often because they are attracted by organic matter inside the trap or because they are influenced by turbulence at the mouth of the trap (Buesseler et al., 2007).

The material collected into the trap is so essentially of two types:

- particles or organisms entered due to gravitative settling, such as fecal pellets, moults, empty shells and algae. All these particles belong to the passive flux;
- organisms coming into the trap alive, the so called swimmers, part of the active flux.

As mentioned above, there are many techniques for removing swimmers, ranging from simple screening with one or more meshes of different sizes to the use of microscopes at different magnifications.

Buesseler (2007) present comparisons between flux measurements by performing two different swimmers removal methods using trap samples from Bermuda and Hawaii. These comparisons have shown great differences in flux results. For example, the carbon flux calculated in the case of picking with a 250X microscope gave values on average 60% lower than in the case of screening done only using sieve.

Removal of swimmers by sieving only can lead to an overestimation of fluxes, while the microscopic hand-picking method can lead to an underestimation because particles of debris may be removed with the swimmers.

It is therefore often important to establish the best protocol for swimmer removal on a site-specific basis.



**Table 2**

Pros and cons of various sample processing method.

Method	Pros	Cons
Swimmer removal by picking under a microscope	You can catalogue all the organisms.	Longer time. Need more operator's experience.
Swimmer removal by screening	Shorter time.	You can not classify the organisms. You can not see some microscopic organisms like foraminifera and radiolarians. Subjectivity.
Splitting with peristaltic pump	Good precision regardless of the operator.	Longer time. Major maintenance. Need a more accurate picking before splitting.
Splitting with folsom plankton splitter	Shorter time. You do not have to do an accurate picking before splitting. No maintenance.	Accuracy depends also on the operator.
Filtering	Less material dispersion.	You have to do a splitting scheme to establish how many and which analysis have to be performed. Samples' pretreatment before the analysis.
Freeze-dry method	You obtain an aliquot of material that you can use like any sediment.	

#### 2.4.2 Swimmers

As already mentioned the presence of organic matter in the sediment trap can attract a large number of organisms (swimmers).

Swimmers sizes may vary from microns to centimeters. It may be difficult to establish the integrity of the soft tissue, and identify any sign of decomposition, elements that allow us to distinguish a dead body that fell into the trap, and therefore part of the passive flux, from an organism that entered alive.

For this reason there are different ways of proceeding: some researchers eliminate only the largest swimmers by using sieves of different mesh sizes to be sure not to pick up organisms belonging to the passive flux (with the risk of overestimating the flux). This methods assumes that the overall impact of the small size class swimmers is negligible. Others consider swimmer removal by hand-picking under a microscope to be the most accurate method of determining the passive sediment flux. Swimmer removal under a microscope allows the processor to distinguish many more organisms that are not be visible to the naked eye. Removing more swimmers may cause a lowering

of Carbon and Nitrogen fluxes. Moreover if you use a peristaltic pump, in which the sample goes into pipes with a diameter of 3 mm, picking under a microscope is appropriate because the pump functioning can be compromised by the presence of many organisms that can clog the pipes.

There are particles, such as eggs, that can enter a trap carried by swimmers. So, even if they are not technically part of the active flux, they must be removed. In general, however, the eggs, for practical reasons, are left in the sample because of the difficulty to remove them without removing other particles (Buesseler et al., 2007).

Microscopic organisms such as bacteria, protozoa and microzooplankton (Radiolarians and Foraminifera) are considered part of the passive flux.

## **2.5 Proposed method**

The method we suggest here is a variation of the method used at ISMAR-CNR Bologna and it is obtained combining this procedure with the treatment of trap samples used at Stanford University. The changes have been made in order to allow for more rapid sample processing without sacrificing precision.

In the following paragraphs we describe the method.

For this method we need 8-10 beakers, a microscope, a 580 micron mesh sieve, forceps, a 2l flask, an orbital shaker, and a peristaltic pump. Furthermore for each sample we need two 125 ml bottles and a 150 ml centrifuge tube.

The aim is to obtain 3 fractions of material, one to keep wet, one dry, and one to be preserved as an archive.

First we let the sample settle for at least one day (more if necessary) until the supernatant is clear and without suspended sediment.

We go on removing the supernatant (as much as possible without touching the sediment), and preserving it in two bottles, 125 ml and 500 ml; the first one will be used to preserve the swimmers taken out from the sample (125 ml) and the other for the sample fraction that will be kept intact as archive (500 ml, you can use for the archive the bottle that contained the total sample). It is important to keep intact the supernatant for measurements such as pH.

We define as swimmers those organisms belonging to the active flux, the ones who "voluntarily" swim into the sediment trap.

After supernatant removal we pour the sample through a 580 micron nylon mesh screen to separate the coarse and fine fractions. For this purpose we have to dilute the sample using filtered sea water from the area of the trap. It is necessary to use sea water from the trap sample location so as to not to modify the chemical composition of the supernatant.

Expected time per sample: 10 to 30 minutes

Now we have two parts of the sample: the coarse fraction (>580 micron) and the fine fraction (<580 micron). We observe both fractions under a stereomicroscope. Using forceps we pick out all swimmers and preserve them in formalin for possible further analysis. At the same time we observe

and catalogue all the large components of the passive flux (fecal pellets, empty shells of crustaceans and other organisms, algae, moults, foraminifera, mucilaginous clusters etc....).

These components are left in the sample.

To preserve the swimmers we use the 125 ml bottle which we have previously filled with the supernatant.

If the sample consists of a large amount of material, the removal of swimmers is done only on the > 580 micron fraction, while picking the swimmers from the fine fraction (<580 micron) is performed only on those splits to be used for analysis. This is a time-saving provision especially useful with large samples.

In order to distinguish the organisms that have swam into the trap from those belonging to the passive flux you have to look respectively at the presence or absence of soft tissue. In some cases this distinction is difficult due to dissolution that can occur within the sample because of poor storage, or due to the nature of some organisms, for example crustacea that have very transparent carapaces. It is evident that this part of analysis is quite subjective and dependent upon the picker. To overcome this problem is therefore appropriate to carry out the picking under a microscope.

Expected time per sample: 1 to 12 hours

We next recombine the two fractions of material (>580 micron and <580 micron) and let the sample settle for supernatant decanting (1 day). When all the particles are settled down we have to remove the excess water being careful not to touch the sample.

Now we proceed with sample splitting to allow us to obtain the right amount of material needed for all analyses. We split the sample into eight parts using the peristaltic pump.

To do this we use a glass flask (2l) containing the sample, an orbital shaker to obtain a suspension as homogeneous as it is possible, and a precision peristaltic pump connected to a mechanical arm that picks up the sample rates of fixed size and put them into beakers prepared for sub-samples.

As mentioned above we produce three fractions of the sample: a freeze-dried, a wet, and a wet archive.

Usually we keep as an archive one half of the sample, we freeze-dried 3/8 of the sample for analyses like silica and carbon, and we store 1/8 of the sample for analyses providing the sample wet. Depending on the size of the sample, these ratios can be changed. In figure 3 it is shown an example of a splitting scheme.

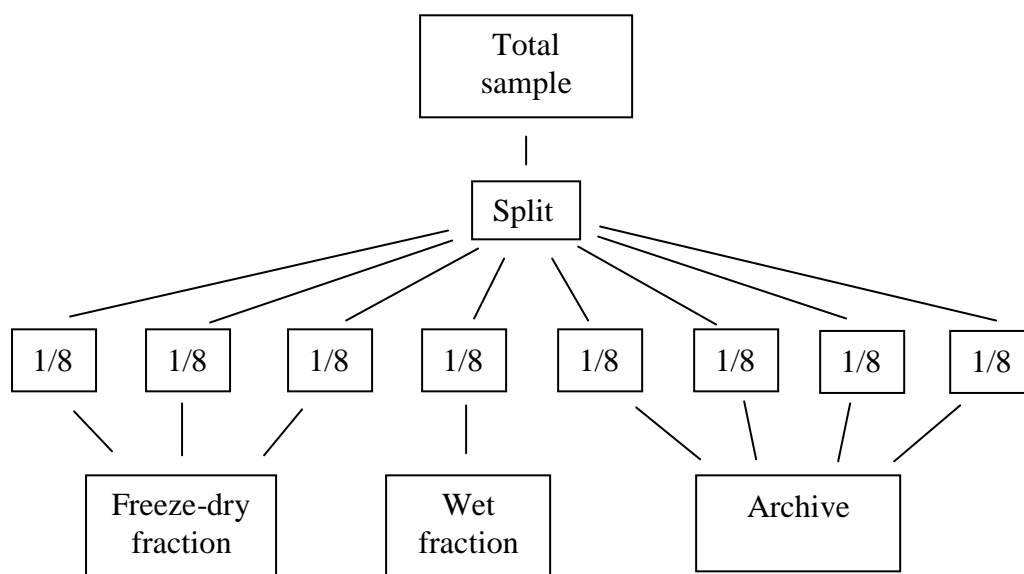
If the sample consists of a large amount of sediment, it may be appropriate to increase the fraction of material to be preserved intact in the archive fraction and use only a smaller part for analyses. It would be desirable to freeze-dry only the sample required for analysis, so that you have an intact archive useful for further investigation. You have to decide how much material you need to use.

Expected time per sample: 1 to 3 hours

Now the subsample fractions are transferred into three bottles. For the archive we can use the original sample bottle in which we have already put the supernatant removed at the beginning of the

operations. The fraction prepared for analysis of wet samples will be transferred to a 125 ml bottle. Further treatments are not carried out on these two fractions, while the third subsample will be subjected to the freeze-dry procedure described below.

Before the freeze-dry procedure swimmers are removed if we have not already done so on the fine fraction sample (as already mentioned).



**Fig. 3.** Example of a splitting scheme using a peristaltic pump.

Freeze-dry procedure:

Let the sample settle for a few days until all suspended material has settled, transfer the sample into centrifuge tubes and follow the instructions below:

1. Place the tube into the centrifuge;
2. centrifuge for 10 minutes at high speed to settle the entire sample at the tube bottom;
3. remove excess water using a syringe;
4. fill the test tube with demineralized water and agitate to resuspend all material to flush salt and formalin from the sediment;
5. centrifuge for 10 minutes and repeat step 3 to 5 for 3 times;
6. let settle for a few days;
7. remove the excess liquid from the tube being careful not to remove sediment also;
8. remove the cap of the tube and dip it into liquid nitrogen to freeze;
9. Place the tube in a freeze dryer until the sample is dry.

The dried fraction will be used for chemical analyses such as: concentration of carbon and nitrogen (as well as their isotopic composition), and weight percentage of biogenic silica, phosphate and carbonate.

After the sample is dried we weigh it and then we grind it to obtain a homogeneous powder. Now we have a fraction of material that can be directly used for the analysis like any sediment.

### 2.5.1 Accuracy

In order to determine the accuracy of the peristaltic pump used (Jencons Perimatic Premier Peristaltic Pump) for the split of sediment trap samples some laboratory tests were carried out.

First of all we determined the accuracy of the dispensed volume. To do this we performed two tests with distilled water. The water was divided into 10 parts each consisting of 20 doses of 2 ml (which is the volume that was used to split the samples). The accuracy achieved (coefficient of variation (C.V.) = standard deviation divided by average value) is 0.17% on average and in both cases less than 0.3%.

Then 3 sets of tests were carried out using about 1 g of fine sediment sample taken from the top of a core so that it was as similar as possible to a sediment trap sample. The sample was dispersed in 500 ml of filtered sea water and divided into different fractions (1/4, 1/6 and 1/8). The experiment was repeated twice for each test.

Each sample, after being weighed dry, was dispersed in 500 ml of filtered sea water and poured into a flask placed on a mechanical stirrer to keep the water and sediment solution as homogeneous as possible. Then the sample was split into a fixed number of subsamples. Each fraction was then transferred into centrifuge test tubes, rinsed with distilled water to remove the sea water salts and centrifuged to allow the sedimentation of all particles. The samples were then placed in a lab oven at 50°C to dry for about 24 hours and then weighed with a balance accuracy of 0.1 mg (and therefore with an error in weighing of 0.2 mg).

The results obtained are shown in table 3; we can see that the C.V. range from 4% for the division into 4 samples to 10% for the subdivision into 8 parts. These percentages obviously take into account the errors that accumulate during the full procedure (e.g. the balance error and the loss of material during the steps).

The loss of material left sticking to the side of containers is approximately constant regardless of the number of fractions and it is on average of 59.6 mg on 1 g of material.

As found by Heussner (1990) errors appear to increase with the number of subsamples per split but, also in this case, the data are not sufficient to determine it for sure.

**Table 3**

Peristaltic pump volumetric and mass precision. For each experiment it is reported the mean coefficient of variation (CV) and the CV range.

Experiment	Level of subsampling	Volume dose (ml)	N. of replicate experiments	N. of measured subsamples/ replicate	Mean CV(%)	CV Range (%)
Volumetric Precision of the pump	1/10	2	2	10	0.17	0.09-0.24
Fine-grained bottom sediment	1/4	2	2	4	4	4
	1/6	2	2	6	6	5-7
	1/8	2	2	8	9.5	9-10
	1/8	1	1	8	6	---

If we use 1 g of sediment in 500 ml of water and we divide the solution into 4 fractions, in each of these there will be about 63 doses of 2 ml each. If the same amount of solution is instead divided into 8 fractions, in each of these we will have about 32 doses of 2 ml.

This means less chance of reducing the effects of random error due to the splitter. To verify the accuracy of this hypothesis, it was thought to repeat the experiment by reducing the single dose from 2 ml to 1 ml so that, by dividing the sample into 8 parts, there are, in each of these, the same amount of doses (about 63) which is obtained by dividing the sample into 4 parts with doses of 2 ml. In this case the error is reduced to 6%, value not equal to that obtained for the splitting in 4 parts (4%) but significantly lower than the one obtained dividing the material into 8 parts with doses of 2 ml.

So the accuracy we have calculated for the Peristaltic Pump is about 6% (considering 6 or 8 subsamples) and it is more or less the same found using the Folsom Plankton Splitter around 5-6% (unpublished data).

## **2.6 Sample processing technique**

The proposed new method does not change the swimmer removal step (with respect to the Heussner procedure) but it does forego the use of filters and the subdivision of the sample in a predefined number of subsamples.

With the Heussner procedure the sample is split many times with a peristaltic pump in order to obtain the right quantities of material for each analysis; this leads to a progressive increase in sample size error with each further subdivision. With the modified method we split the sample only one time thereby reducing this error and obtaining a precision similar to that obtained by the Folsom Plankton Splitter.

Since swimmer removal is the step that is most likely to influence the flux values, the difference between the proposed method and the Heussner procedure consists on the accuracy and the two methods are perfectly compatible.

It was not possible to perform a direct comparison between the three methods (Stanford, Heussner and Heussner method modified) because our samples were too small. So we have compared the results obtained with the three different methods on samples from different years in two areas; we have observed that the results are comparable taking into account the inter-annual variability that characterizes these areas. The percentage contribution due to the swimmers can not be absolutely quantified in because it depends on the sample analyzed. For example, Collier et al. (2000) found a range from 5% to 90% in the potential contribution of swimmers to the Organic Carbon flux on different samples – if they were not removed via picking.

Inter-annual variability affects the magnitude of sediment fluxes and the periods of maximum sediment accumulation. However, many features of the particle flux exhibit minimal variability. Usually particle fluxes exhibit a maximum peak during the ice melting period in summer, another one during the ice formation, at the end of summer, and lower values, close to zero, in winter. Furthermore during summer the collected material is about 50% of the entire year one.

In table 4 and table 5 we report the organic carbon fluxes ranges related to the mooring B (MB) and mooring A (MA) samples respectively. We can observe that the results are comparable with one

another taking into account the inter-annual variability of this region documented in literature (Dunbar et al., 1998; Collier et al., 2000; Buesseler et al., 2007); in fact, we see that even between samples treated with the same method (Heussner method) (Table 4), the minimum values obtained for the top trap goes from 0 to 4.61 mg/(m<sup>2</sup>d) and the maximum from 7.8 to 39.75 mg/(m<sup>2</sup>d) while for the bottom trap we have minimum values between 0.7 and 1.60 mg/(m<sup>2</sup>d) and maximum values from 12.80 to 19.0 mg/(m<sup>2</sup>d). The values obtained on the MB 2008 samples treated with the Heussner method modified show a range compatible with the ones treated with Heussner method (Table 4). With regard to the anomalous maximum value reached in MB 2005, it occurs in a sampling period in which it was found a high abundance of the specie *Limacina helicina* in conjunction with a high mass flux while the other high values of organic carbon fluxes are around 20 mg/(m<sup>2</sup>d) (Chiarini et al., in prep. (chapter 4)).

In table 5 mooring A samples related to 2005 and 2008 and processed with Heussner modified and Stanford methods respectively have been compared. Minimum and maximum values for the upper water column trap are similar. However, fluxes differ significantly at the bottom but this is related to variations in lateral advection processes during different years (Chiarini et al., in prep. (chapter 5)).

**Table 4**

Comparison between Site B organic carbon flux range for samples treated with Heussner (1990) and Heussner modified methods. MB: mooring B investigated site.

Site	Level	OC fluxes range (mg/(m <sup>2</sup> d))	Method
MB 1995	Top	0-7.8	Heussner et al. (1990)
	Bottom	1.5-19.0	
MB 1996	Top	0.05-14.1	Heussner et al. (1990)
MB 1998	Top	0.7-22	Heussner et al. (1990)
	Bottom	0.7-15.1	
MB 1999	Top	4.61-39.75	Heussner et al. (1990)
	Bottom	1.60-12.80	
MB 2005	Bottom	3.32-53.85	Heussner (modified)
MB 2008	Bottom	0.002-19.53	Heussner (modified)

**Table 5**

Comparison between Site A organic carbon flux ranges for samples treated with Heussner modified and Stanford methods. MA: Mooring A investigated site.

Site	Level	OC fluxes range (mg/(m <sup>2</sup> d))	Method
MA 2005	Top	0.05-35.87	Heussner (modified)
	Bottom	1.29-35.56	
MA 2008	Top	0.75-33.44	Stanford (laboratory)
	Bottom	0.82-19.00	

## 2.7 Conclusions

In this paper we present a sediment trap sample processing method in order to improve the procedure used at ISMAR-CNR Bologna based on Heussner method. This methodology combines the laboratory procedures adopted at the ISMAR Institute and at Stanford University.

Fluxes values may be influenced by the contribution of organisms belonging to the active flux (swimmers). Since we have not changed the swimmer removal step, the proposed new method and the Heussner procedure are comparable.

In particular we propose to remove swimmers using a microscope (only on a portion of the sample for large amounts of trapped material), to use a Peristaltic Pump but only to obtain a fraction to freeze-dry taking off the use of filters. This method has the advantage of combining precision and speed.

With respect to the method used at ISMAR-CNR, the changes are mainly related to the splitting methodologies and the adoption of freeze-drying.

One of the aims of modifying the well tested method used at ISMAR-CNR was to make it faster. Sometimes this has been possible, other times we decided not to reduce precision in favour of speed.

Removing swimmers under a microscope takes a long time but this method is the most accurate. The accuracy depends on the experience of the picker. It is also true that it is more difficult to distinguish active from passive flux if the organisms are microscopic. Using a microscope you are able to catalogue all the components present in the sample, including moults, algae and microscopic organisms such as foraminifera. This can provide you additional information on biological dynamics.

It is possible to remove swimmers only with the help of a magnifying glass, but in this case only the larger organisms would be removed. It would also be impossible to correctly classify the organisms present.

While you are removing swimmers you can also find foreign materials such as textile fibres or metal parts that come from the mooring. The analysis under the microscope is more suitable because you can recognize and remove them.

We think that to obtain the most accurate results it is appropriate to use a microscope, although this obviously makes this phase longer and more laborious.

The use of the Peristaltic Pump instead of Folsom Plankton Splitter make the splitting less subjected to the operator experience even if it takes slightly longer time and the instrument needs more maintenance and attention (need to dilute the sample, with time increase, to prevent algae, clusters mucilage and pteropods can clog pipes) and a more accurate picking. With our modified method the accuracy is about 6%, like that of the Folsom Plankton Splitter, because we split the sample only once so as to eliminate the errors propagation.

The freeze-dry method requires a shorter time than using filters. The samples are no longer on filters but we get a dried aliquot of sample that, after grinding, can be used in the analysis as any sediment.

Putting the samples on filters we need to make the pre-treatment before the analysis; drying the sample directly it is not necessary to make the pre-treatment that can increase the error.



We are not compelled by the a priori choices made with the splitting scheme about the number and type of analysis to be done. In contrast, the placement on filters prevents possible losses of material depending on the accuracy of the operator but we think that the advantages exceed the disadvantages.

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## Chapter 3\*

# Seasonal variability of biogenic and mass fluxes in the Ross Sea (Antarctica): results from sediment traps collection

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### 3.1 Abstract

In this paper we present data about biogenic fluxes (biosilica, organic carbon and nitrogen) related to sediment trap samples positioned in two different sites of the Ross Sea (site A: 76°41'S - 169°02'E and site B: 74°00'S - 175°05'E) during 2008. In this area the values obtained document spatial and temporal fluxes variability. At site A mass fluxes ranged from 5.0 to 409.6 mg/(m<sup>2</sup>d) at the top trap and from 6.8 to 226.1 mg/(m<sup>2</sup>d) at the bottom, biogenic silica fluxes ranged from 0.42 to 1441.17 mg/(m<sup>2</sup>d) and from 1.01 to 80.44 mg/(m<sup>2</sup>d) respectively at the top and at the lower level and Organic Carbon fluxes varied from 0.75 to 33.44 mg/(m<sup>2</sup>d) and from 0.82 to 19.00 mg/(m<sup>2</sup>d) at the two levels. At site B the values obtained at the bottom level for biogenic silica fluxes were lower, ranging from 0 to 58.06 mg/(m<sup>2</sup>d) while they were higher for organic carbon ranging from 0.01 to 115.03 mg/(m<sup>2</sup>d). We have compared mass and biogenic fluxes to underline the differences between the two sites relating them with ice coverage and chlorophyll a concentration data to investigate the causes of seasonal variability.

### 3.2 Introduction

Polar environments are the most important sites where occur changes between atmosphere and ocean due to the low temperature that favours the absorption processes of atmospheric gases, especially CO<sub>2</sub> (Takahashi et al., 2002). For this reason, the alterations of biogeochemical cycles in these areas impact on climate at global scale. The ocean ability to export the dissolved CO<sub>2</sub> through the C absorption due to the biomass (biological pump) is crucial for the CO<sub>2</sub> exchanges between ocean and atmosphere (Jahnke, 1990).

Particle fluxes control the carbon transfer from surface waters to the deep ones, the nutrient regeneration, the transport of nutrients to benthic communities and the preservation of sedimentary records that testify the climate change (Dunbar et al., 1998; Arrigo et al., 1999).

In the Southern Ocean zooplankton grazing and recycling/regeneration processes along the water column affect particle fluxes. Moreover carbon and biogenic fluxes changes are related to wind, oceanic circulation, sea ice and cloud cover which influence primary productivity (Arrigo et al., 1998).

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\* This chapter consists of a paper in preparation by Chiarini F., Capotondi L., Giglio F., Langone, L., Ravaioli, M., "Seasonal variability of biogenic and mass fluxes in the Ross Sea (Antarctica): results from sediment traps collection"

The Ross Sea is one of the most productive areas in Antarctica (Tremblay and Smith, 2007), and it is important both for the ocean absorption of atmospheric carbon (Arrigo et al., 2008) both for the study of biogeochemical cycles.

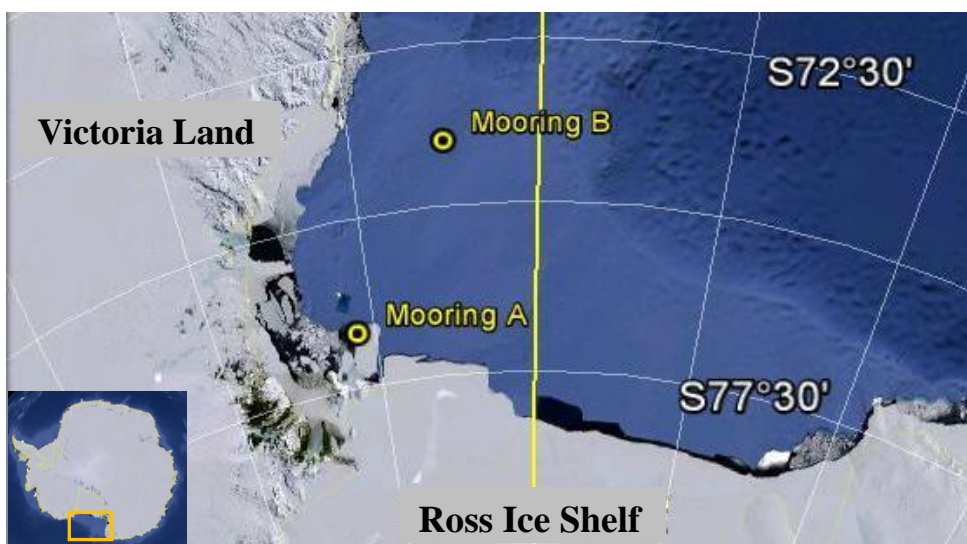
This study is part of the project ABIOCLEAR – biogeochemical cycles in Antarctica – climatic and paleoclimatic reconstructions, focused on the study of biogeochemical cycles of C and Si in the Southern Ocean, to estimate their export rates in a particular area of the Ross Sea and in some sites of the Southern Ocean.

The Ross Sea presents a high temporal and regional variability: the first due mainly to the expansion and retreat of sea ice, the second to the presence of different groups of organisms. The south-western area is characterized by intense diatom blooms, it has the highest accumulation rates and surface sediments with the highest biogenic silica content and it is the sector first free from ice cover; the central area is dominated by *Phaeocystis antarctica* and the south-eastern is again dominated by diatoms. Finally, the northern area, dominated by diatoms, has the lowest productivity of the Ross Ice Shelf because of the greater permanence of ice compared to other sectors (Smith et al., 1996).

The ice retreat begins during the austral spring from the southern polynia extending to the north, so the algal bloom will occur first in the south and south-west regions and then in the northern one. The Ross Sea has thus two main positive gradients in primary productivity: N-S and E-W.

In this paper we present the results of the analyses of particles collected in 2008 in two sites (A and B) of the Ross Sea (Fig. 1). In particular mooring A (MA) is located in a polynia area bordering the ice-shelf, one of the areas with the greatest primary productivity of the Ross Sea; instead mooring B (MB) is placed in the Joides Basin, an area characterized by high accumulation of bio-silica sediments and by the presence of significant processes of lateral advection.

In order to point out the main differences between these two areas, we analyzed the vertical fluxes of biogenic silica, organic carbon and nitrogen. Moreover, we compared the fluxes data with the extension and the concentration of sea ice and with the concentration of chlorophyll a.



**Figure 1:** position of mooring A and B in the Ross Sea. Yellow line represents the antemeridian.

### 3.3 Productivity in the Ross Sea

The Ross Sea shows, like all the antarctic continental shelves, the highest values of productivity of the Southern Ocean.

Primary productivity in the Ross Sea is affected by seasonal changes due to solar radiation, wind and ice extent. So it is low during the late austral winter and early austral spring.

Many field studies have documented high inter-annual variability in phytoplankton biomass production (Collier et al., 2000; Arrigo and van Dijken, 2004) and phytoplankton composition (Smith et al., 2006) in addition to the seasonal variability usually characterized by an unimodal bloom and sometimes a secondary bloom comparable in size to the primary one (Peloquin and Smith, 2007). Usually the phytoplankton in this area is mainly composed by diatoms which variations exert an high control on the export rates (Boyd and Newton, 1999; Armstrong et al., 2009).

Changes in the composition and magnitude of phytoplankton, in addition to lateral advection and mixing processes, have a strong impact on biogeochemical fluxes implying a short-term variability.

The Ross Sea polynia is generated by strong winds that blow away the ice, which forms near the coast, from the continent to the open sea (Gordon and Comiso, 1988). This polynia starts to form in November and so the phytoplankton bloom may begin during this period when other coastal regions are still covered by ice.

From October through December the solar radiation increases and consequently the productivity raises both in the ice and in open sea areas.

Organic carbon in this region is mainly produced in the open sea areas of south western Ross Sea. The annual primary productivity goes from 91 gC/(m<sup>2</sup>yr) in the northern area to 216 gC/(m<sup>2</sup>yr) in the southern one (Nelson et al., 1996).

### 3.4 Materials and methods

Two moorings were deployed in the Ross Sea in the frame of the ABIOCLEAR project on January 2008. Mooring A was deployed in the SW Ross Sea at 76°41'S - 169°02'E (832 m water depth) in the Ross polynia near the ice edge during the austral summer. This area is characterized by high primary productivity for the presence of diatoms seasonal blooms and the reduction of ice cover that occurs, usually, in December with the expansion of the polynia.

Mooring B was deployed in the northern part of the Joides Basin at 74°00'S – 175°05'E (604 m water depth). The Joides Basin is a shelf basin with SW-NE direction. In the central part of the basin fine sediments that fall from the neighbouring banks can be find (Labbrozzi et al., 1998).

Each mooring was equipped with two sets of instruments, each consisting of a time-series McLane sediment trap (with 13 bottles in the Mooring A and with 21 bottles in the Mooring B for each level), a SeaCat CTD recorder SBE16 plus and an Aandera RCM9 current meter.

The two sets of instruments have been placed in mooring A at 370 and 780 m below the sea level and in mooring B at 235 and 550 m below the sea level.

The top level of tools allows to measure the characteristics of particles flux exported from the euphotic zone. The bottom level to estimate the lateral advection, resuspension, scouring and degradation/dissolution processes.

Sediment trap sampling intervals were synchronous between top and bottom traps and ranged from 7 days to 4 months. The differences in sampling intervals are due to the need of obtaining a higher resolution during periods of increased primary productivity. The instruments worked quite well, completing the acquisition data and the sampling program, despite a 2 years period into the sea (the moorings were deployed on February 2008 and taken out on January 2010). Due to a mechanical failure the top trap of the mooring B collected the entire sediment into a single bottle.

Samples were prepared for analysis in two different laboratories: the mooring A samples at Stanford University (California) and the mooring B ones at ISMAR CNR in Bologna (Heussner method modified described in chapter 2). The methods used have some differences related to the splitting method and the swimmers removal but they are comparable (Chiarini et al., submitted (Chapter 2)). First of all we have removed part of the supernatant to preserve it. Then we have filtered the sample with a 580 microns mesh (only with the Heussner method modified) to sort out the coarse sediment from the finest.

Before proceeding with the splitting, we have removed the larger size swimmer that may block the peristaltic pump (only with the Heussner method modified), then we have splitted the sample (with a Folsom Plankton Splitter at Stanford and with a precision Peristaltic Pump at ISMAR) to obtain three different fractions of material, depending on the initial abundance of the sample, one of which was held as an archive, one was kept wet and another was freeze-dried.

An accurate picking has been carried out under a stereomicroscope (Heussner method modified) on the fraction of sample to be dried. The samples obtained were used for biogenic silica, carbon and nitrogen analysis.

The steps of the two procedures for the sediment trap samples are briefly summarized in table 1.

**Table 1:** description of the two different procedures used for the treatment of the samples

<b>MA 2008</b>	<b>MB 2008</b>
1. Remove the supernatant	1. Remove the supernatant
2. Split the sample with a Folsom Plankton Splitter many times until you have obtained the right quantity of material	2. Filter the sample with a 580 micron mesh
3. Make the picking with a magnifying glass only on the fraction to be used for the analysis	3. Make the picking with a microscope to remove the larger swimmers
4. Centrifuge the fraction addressed for the analysis and dry it with a freeze-dry procedure	4. Split the sample in 8 parts with a peristaltic pump
	5. Make the picking under a microscope
	6. Put the 8 parts you have obtained with the splitting together to obtain 3 fractions: an archive, a fraction to be dried and a fraction to be preserved wet
	7. Freeze-dry the fraction to be dried

The content of biogenic silica was obtained by the dissolution method suggested by DeMaster (1981). The total content of nitrogen and organic carbon were determined using a CHN analyzer. We used the following relations to evaluate the composition of the particulate matter:

$$\begin{aligned}\% \text{CaCO}_3 &= (\% \text{C}_{\text{tot}} - \% \text{C}_{\text{org}}) * 8.33 \\ \% \text{lithogenics} &= 100 - (\% \text{C}_{\text{org}} * 2) - \% \text{CaCO}_3 - \% \text{BioSi} - \% \text{N}_{\text{tot}}\end{aligned}$$

Sea ice concentration, which is the percentage of ocean covered by sea ice, has been derived from the final daily data made available by the National Snow and Ice Data Center, obtained with the DMSP-F17 Special Sensor Microwave Imager/Sounder (SSMIS). This sensor has a resolution of 25 X 25 km<sup>2</sup> and the ice concentrations data represents a daily average on a grid cell. These data are generated using the NASA Team algorithm. The stereographic projection uses a projection plane at 70 degrees southern latitude. The planar grid so obtained has the nominal resolution at 70 degrees and present a maximum distortion of 22 percent.

Chlorophyll a (Chl a) concentrations were derived from Moderate Resolution Imaging Spectroradiometer (MODIS) sensor on the Aqua satellite (4 km resolution). Data have been processed using the Giovanni online data system, developed and maintained by the NASA GES DISC.

To compare Chl a and sea ice concentrations we have considered for each mooring the smallest area that contains the grid cell used by the National Snow and Ice Data Center. The average value of Chl a are related for each mooring to the areas which boundaries are reported in table 2.

**Table 2:** Boundaries of the areas on which Chl a has been averaged

	Lat	Lat	Lon	Lon
Mooring A	76.60°S	76.89°S	167.87°E	169.105°E
Mooring B	73.88°S	74.14°S	175.01°E	175.92°E

## 3.5 Results

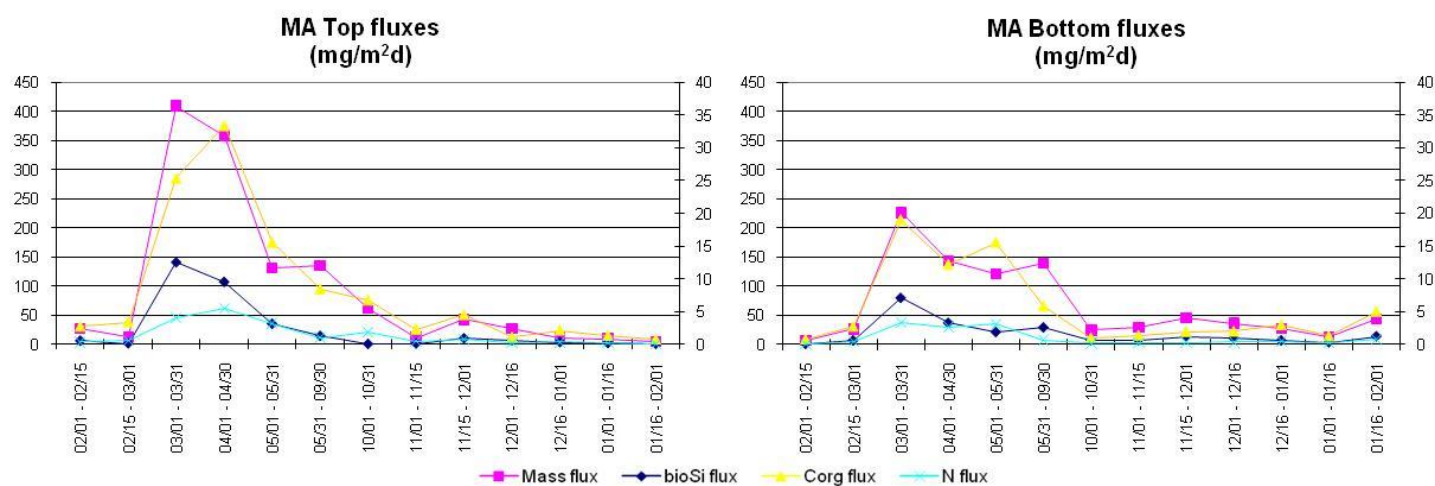
### 3.5.1 Particle fluxes

#### Mooring A 2008

The total mass flux during the year was 47.8 g/(m<sup>2</sup>yr) in the surface trap and it was 36.1 g/(m<sup>2</sup>yr) in the bottom trap. Mass flux values were higher in March with a peak of 409.6 mg/(m<sup>2</sup>d) in the top trap and 226.1 mg/(m<sup>2</sup>d) in the bottom trap.

The top trap presented mass flux highest values from March to April and a drastic decreasing in May. In the bottom trap the mass flux remained quite high from March to September, even if from May the values were lower (Fig. 2).





**Figure 2:** Mass , BioSi, Corg and Nitrogen fluxes time series at mooring A (top and bottom traps). Primary vertical axis values (on the left) for mass and bio silica fluxes (mg/m<sup>2</sup>d), secondary axis (on the right) for Corg and N fluxes (mg/m<sup>2</sup>d)

Organic carbon concentrations ranged from 4.0% to 25.2% in the top trap and from 4.2% to 12.8% in the bottom trap (Table 3). Biogenic silica contents ranged from 0.7% to 34.5% in the top trap and from 14.9% to 35.6% in the bottom trap. Nitrogen concentrations ranged from 0.7% to 4.5% at the top trap and from 0.5% to 2.5% at the bottom trap. The annual mean of C/N molar ratio was about the same in both traps (7.5 – 7.6) and the mean of SiO<sub>2</sub>/OC molar ratio increased from 0.4 at the surface to 0.9 at the bottom.

Organic carbon and opal fluxes trend were similar to total mass flux trend along the entire year (Fig. 2). At the surface level maximum values were 141.2 mg/(m<sup>2</sup>d) for biogenic silica, 32.4 mg/(m<sup>2</sup>d) for organic carbon and 5.4 mg/(m<sup>2</sup>d) for nitrogen. In the bottom trap maximum values were 80.4 mg/(m<sup>2</sup>d) for biogenic silica, 19.0 mg/(m<sup>2</sup>d) for organic carbon and 3.4 mg/(m<sup>2</sup>d) for nitrogen.

The highest values of organic carbon occurred in April in the top trap, in March in the bottom trap. The highest fluxes of biogenic silica also occurred in March in both traps.

**Table 3:** Mooring A mass and biogenic fluxes and per cent values of organic carbon, total nitrogen and biogenic silica in the trap samples.

Sample	Start	Stop	Days	Total flux (mg/m <sup>2</sup> d)	%C org	%SiO <sub>2</sub> biogenic	%N	C flux (mg/m <sup>2</sup> d)	Si flux (mg/m <sup>2</sup> d)
Top 1	02/01/2008	02/15/2008	15	27.4	10.0	21.5	1.3	2.8	5.9
Top 2	02/15/2008	03/01/2008	14	14.5	25.2	9.3	4.5	3.4	1.3
Top 3	03/01/2008	03/31/2008	30	409.6	6.2	34.5	1.0	25.4	141.2
Top 4	03/31/2008	04/31/2008	31	346.8	9.3	31.0	1.5	33.4	107.4
Top 5	04/31/2008	05/31/2008	31	131.4	11.9	26.8	2.5	15.6	35.2
Top 6	05/31/2008	09/30/2008	122	135.1	6.3	10.6	0.8	8.5	14.3
Top 7	09/30/2008	11/01/2008	32	60.2	10.8	0.7	3.1	6.7	0.4
Top 8	11/01/2008	11/15/2008	14	11.8	19.4	10.0	4.4	2.3	1.2
Top 9	11/15/2008	12/01/2008	16	42.7	10.6	23.4	1.9	4.5	10.0
Top 10	12/01/2008	12/16/2008	15	27.7	4.0	25.1	0.7	1.1	7.0
Top 11	12/16/2008	01/01/2009	16	11.7	18.3	30.2	3.1	2.1	3.5
Top 12	01/01/2009	01/16/2009	15	9.6	13.9	20.4	2.3	1.3	2.0

Top 13	01/16/2009	02/01/2009	16	5.0	15.0	11.1	2.1	0.8	0.6
Bot 1	02/01/2008	02/15/2008	15	6.8	12.1	14.9	1.9	0.8	1.0
Bot 2	02/15/2008	03/01/2008	14	28.6	10.4	24.9	1.6	2.8	7.1
Bot 3	03/01/2008	03/31/2008	30	226.1	8.4	35.6	1.5	19.0	80.4
Bot 4	03/31/2008	04/31/2008	31	138.3	8.5	27.0	1.9	12.2	37.4
Bot 5	04/31/2008	05/31/2008	31	121.3	12.8	17.7	2.5	15.6	21.5
Bot 6	05/31/2008	09/31/2008	122	139.3	4.2	21.2	0.5	5.9	29.5
Bot 7	09/31/2008	11/01/2008	32	23.8	4.3	32.1	0.8	1.1	7.6
Bot 8	11/01/2008	11/15/2008	14	29.3	4.8	26.6	0.8	1.4	7.8
Bot 9	11/15/2008	12/01/2008	16	46.3	4.2	30.5	0.8	2.0	14.2
Bot 10	12/01/2008	12/16/2008	15	36.6	5.5	30.9	1.0	2.0	11.3
Bot 11	12/16/2008	01/01/2009	16	27.3	11.0	25.8	1.9	3.0	7.1
Bot 12	01/01/2009	01/16/2009	15	13.9	9.3	26.8	1.5	1.3	3.7
Bot 13	01/16/2009	02/01/2009	16	43.3	11.7	32.8	1.8	5.1	14.2

### Mooring B 2008

Only for the bottom trap it has been counted the mass integrated over the sampling days (22.6 g/m<sup>2</sup>) and the annual flux of silica (3.0 g/(m<sup>2</sup>yr)). The percentage of silica ranged from 0% to 64.5% with a mean value of 4.5% in the top trap. Table 4 shows the values obtained for each sample.

The gaps are due to the impossibility in some cases to perform the laboratory tests due to the shortage of the bottom samples (8, 11, 13, 15, 16, 17, 18). Because of a failure the top trap collected the sediments of about two years in a single cup.

In the bottom trap mass flux values were higher in March-April with a peak of 609.2 mg/(m<sup>2</sup>d) and they decreased dramatically in May becoming quite null until September.

**Table 4:** Mooring B mass and biogenic fluxes and per cent values of organic carbon, total nitrogen and biogenic silica in the trap samples

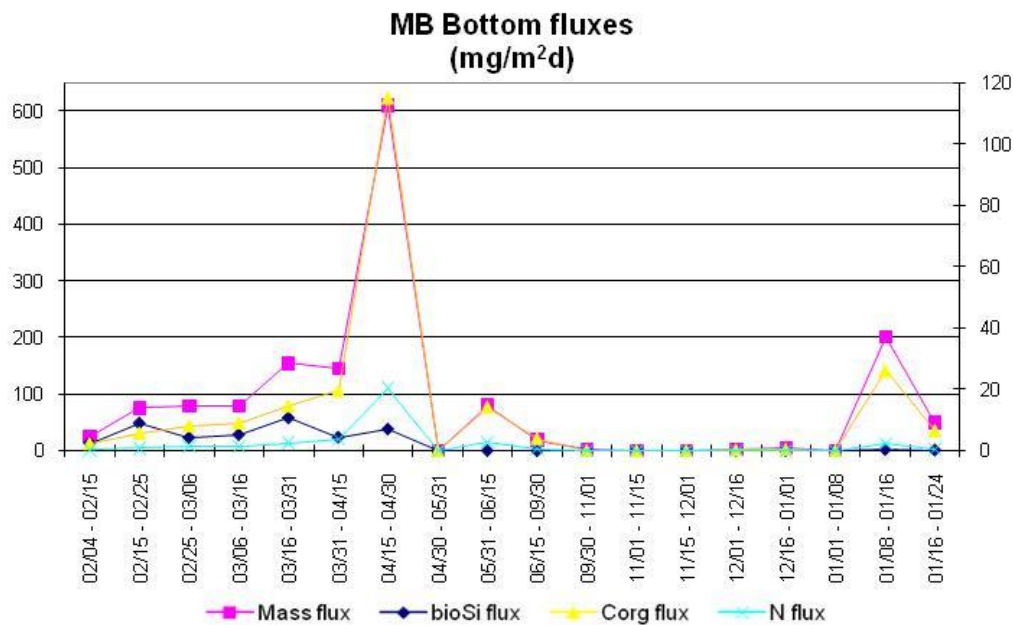
Sample	Start	Stop	Days	Total flux (mg/m <sup>2</sup> *d)	%C org	%SiO <sub>2</sub> biogenic	%N	C flux (mg/m <sup>2</sup> d)	Si flux (mg/m <sup>2</sup> d)
Top 1	2/4/2008	1/1/2010	697	16.7	3.4	4.5	0.5	0.6	0.7
Bot 1	2/4/2008	2/15/2008	11	25.4	9.0	54.0	1.2	2.3	13.7
Bot 2	2/15/2008	2/25/2008	10	75.2	7.6	64.5	1.0	5.7	48.5
Bot 3	2/25/2008	3/6/2008	10	78.2	10.5	29.6	1.7	8.2	23.2
Bot 4	3/6/2008	3/16/2008	10	78.4	11.6	36.3	1.8	9.1	28.5
Bot 5	3/16/2008	3/31/2008	15	154.2	9.4	37.6	1.7	14.5	58.1
Bot 6	3/31/2008	4/15/2008	15	144.5	13.5	16.5	2.6	19.5	23.9
Bot 7	4/15/2008	4/31/2008	15	609.2	18.9	6.3	3.4	115.0	38.2
Bot 8	4/31/2008	5/31/2008	31	0.1	19.3	----	3.3	0.0	----
Bot 9	5/31/2008	6/15/2008	15	79.7	21.3	0.0	3.6	17.0	0.0
Bot 10	6/15/2008	9/31/2008	107	18.9	20.7	0.0	3.4	3.9	0.0
Bot 11	9/31/2008	11/1/2008	32	1.6	9.4	----	1.4	0.2	----
Bot 12	11/1/2008	11/15/2008	14	-----	----	-----	----	----	-----
Bot 13	11/15/2008	12/1/2008	16	0.3	12.1	----	2.1	0.0	----
Bot 14	12/1/2008	12/16/2008	15	-----	----	-----	----	----	-----
Bot 15	12/16/2008	1/1/2009	16	0.1	6.7	----	1.7	0.0	----

Bot 16	1/1/2009	1/8/2009	7	2.2	11.1	----	1.6	0.3	----
Bot 17	1/8/2009	1/16/2009	8	4.3	9.7	----	1.4	0.4	----
Bot 18	1/16/2009	1/24/2009	8	0.5	4.8	----	0.8	0.0	----
Bot 19	1/24/2009	2/1/2009	8	201.5	7.4	1.0	1.2	15.0	2.0
Bot 20	2/1/2009	3/1/2009	28	49.3	6.9	2.2	1.1	3.4	1.1
Bot 21	3/1/2009	1/1/2010	306	0.0	19.0	----	3.3	0.0	----

Organic carbon concentrations ranged from 6.7% to 21.3% in the bottom trap with a mean value of 3.4% for the entire sampling period in the top trap (Table 4). Nitrogen concentrations ranged from 0.8% to 3.6% at the bottom trap with a mean value of 0.5% in the top trap. The annual mean of C/N molar ratio was 7.8 at the top trap and 7.2 at the bottom; the mean of  $\text{SiO}_2/\text{OC}$  molar ratio increased from 0.1 at the surface to 0.2 at the bottom.

During the entire year organic carbon and opal fluxes trend followed the total mass flux one (Fig. 3). In the bottom trap maximum values were 58.1  $\text{mg}/(\text{m}^2\text{d})$  for biogenic silica, 115.0  $\text{mg}/(\text{m}^2\text{d})$  for organic carbon and 20.4  $\text{mg}/(\text{m}^2\text{d})$  for nitrogen. The highest values of organic carbon and biogenic silica occurred respectively in April and in March.

In table 5 we report the annual (366 days) integrated fluxes calculated at the two sites .



**Figure 3:** Mass, BioSi, Corg and Nitrogen fluxes time series at mooring B (bottom trap). Primary vertical axis values (on the left) for mass and bio silica fluxes ( $\text{mg}/\text{m}^2\text{d}$ ), secondary axis for Corg and N fluxes ( $\text{mg}/\text{m}^2\text{d}$ )

**Table 5:** Annual integrated fluxes at the two sites. (\* total fluxes on 697 days; \*\*discontinuous time series)

Site	Integrated mass flux $\text{g}/(\text{m}^2\text{yr})$	Integrated C flux $\text{g}/(\text{m}^2\text{yr})$	Integrated bio Si flux $\text{g}/(\text{m}^2\text{yr})$	Integrated N flux $\text{g}/(\text{m}^2\text{yr})$
MA 2008 top	47.8	3.8	10.8	0.6
MA 2008 bottom	36.1	2.5	9.1	0.4
MB 2008 top	11.6*	0.4*	0.5*	0.06*
MB 2008 bottom	22.8	3.4	2.8**	0.6

### 3.5.2 Sample composition

At both sites the most abundant organisms found in the samples were pteropods, belonging to the *Limacina helicina* species, with a maximum of 11400 specimens (MB) in the first two weeks of June, followed by various types of crustaceans such as amphipods and copepods.

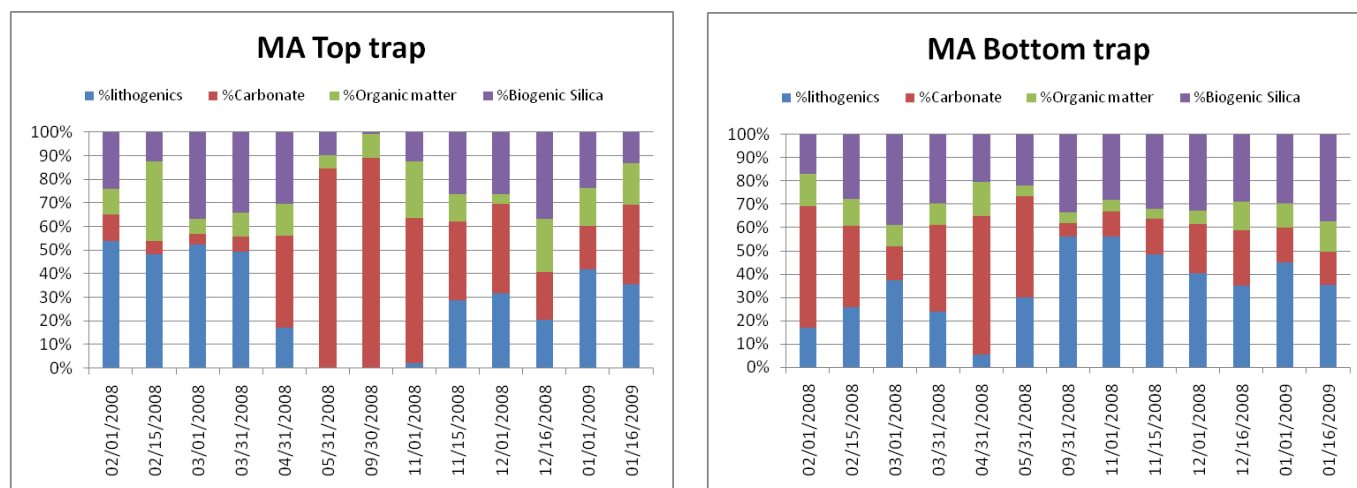
In the samples of site B we found some specimens of foraminifera (especially of the species *Neogloquadrina pachyderma dextral*) mainly between March and April 2008, and between January and February of the following year. The samples of mooring A were not observed under the microscope and it was thus impossible to distinguish smaller organisms like foraminifera.

With the exception of the 2008 peak of foraminifera found in April, the period of maximum flux of organisms was from June to September.

We also found some fecal pellets (most abundant in the months of increased flux of organisms) of various shapes and color, some light and elongated maybe derived from copepods and other round and dark.

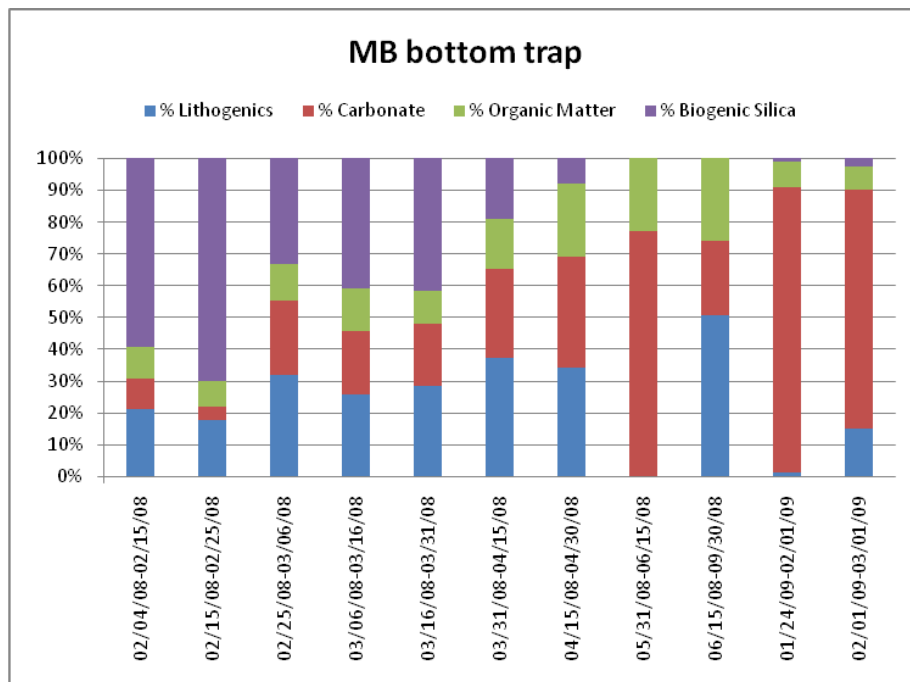
At site A the percentage composition of the top trap samples shown quite variable values for all elements with a high percentage of carbonates from June to mid-November.

In the bottom trap the percentages of bio-silica and organic carbon were more constant and even the values of the lithogenic component were constant in the second part of the year. The percentage of carbonate, instead, showed values significantly higher than the top trap values in the first half of the year (Fig. 4).



**Figure 4:** Percentage composition of the samples of mooring A (top and bottom traps)

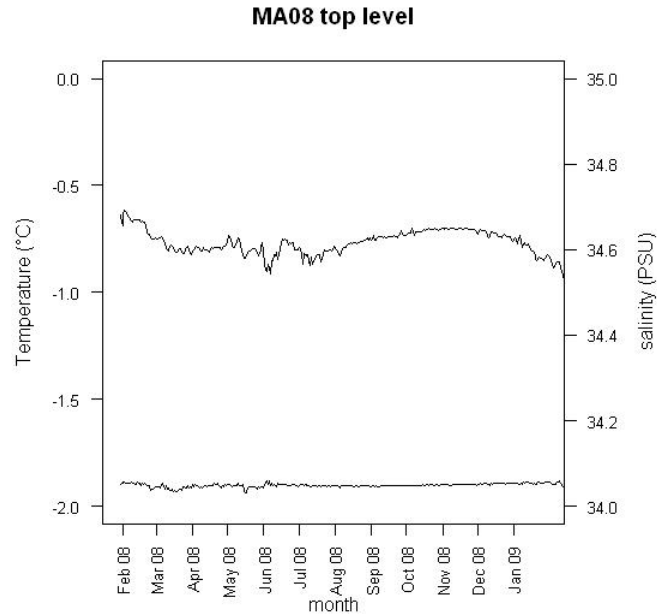
The percentage composition of the bottom trap samples collected in site B (Fig. 5) showed a high variability. The percentage of biogenic silica decreased during the year to a minimum of 0% from June to September. Even in this case high percentages of carbonates were observed in June 2008 (as at site A) and in January and February of the following year.



**Figure 5:** Percentage composition of the bottom trap samples at mooring B

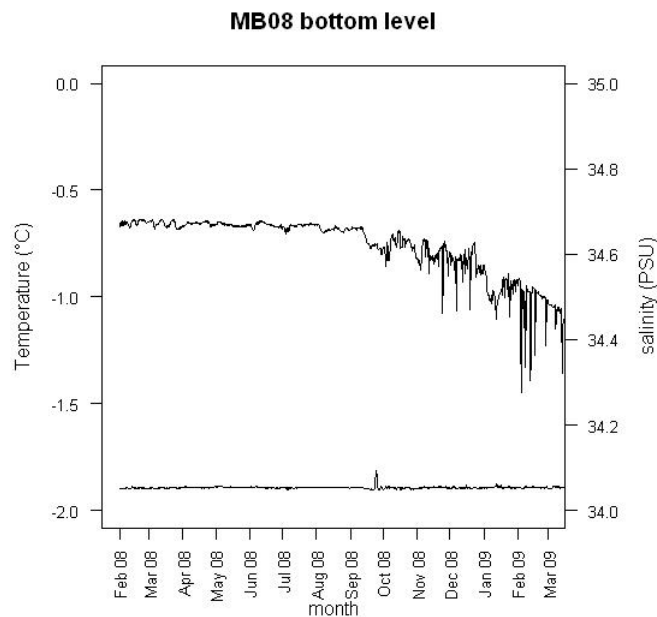
### 3.5.3 Physical parameters

The temperature values recorded at 370 m at site A were quite constant during mid June through December 2008 with values around  $-1.9^{\circ}\text{C}$  (min  $-1.91^{\circ}\text{C}$ , max  $-1.89^{\circ}\text{C}$ ). From February to May 2008 the temperature records exhibited little excursions (mean  $-1.91^{\circ}\text{C}$ , max  $-1.88^{\circ}\text{C}$ , min  $-1.94^{\circ}\text{C}$ ). The salinity maximum value (34.69) was reached in February. The salinity values decreased until March, they varied from March to June around 34.60, they increased until November and then they decreased again (Fig. 6).



**Figure 6:** Temperature and salinity trend at the top level of site A during 2008

The temperatures recorded throughout the year at the bottom level (534 m) in site B had a uniform value of about  $-1.89^{\circ}\text{C}$  (min  $-1.91^{\circ}\text{C}$ , mean  $-1.89^{\circ}\text{C}$ , max  $-1.81^{\circ}\text{C}$ ). The salinity records presented for half the year fairly constant values around 34.67 (max 34.68, min 34.65) and they became lower and unstable from the beginning of October (Fig. 7). During November 2008 through March 2009 they presented rapid excursions and a decreasing trend, reaching values of 34.30 (max 34.66, min 34.28, mean 34.55).

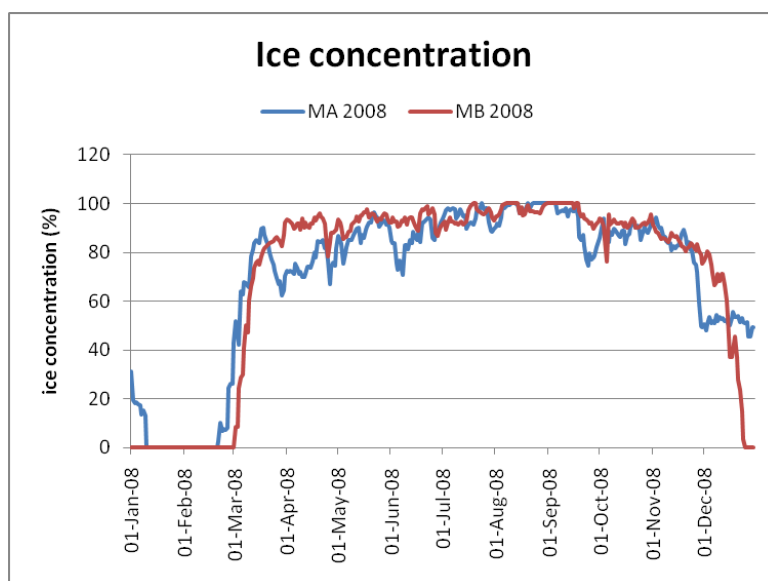


**Figure 7:** Temperature and salinity trend at site B

### 3.5.4 Sea ice concentrations

The MA area was completely ice free for a period of 40 days (from January 10 to February 20), with a sea ice concentration below 50% from January 1 to 10 and from February 20 to March 4. In March, there was a rapid closure of the polynia. From April, the concentration showed large oscillations around 90% (Fig. 8).

At site B the period in which the ice was totally melted lasted 2 months (from January 1 to March 1), there were ice concentration values below 50% for a few days, from March 2 to 9, and then a rapid growth of percentages up to values close to 100% since the end of March. From April the ice concentration remained stable around 90% with little fluctuations. Towards the end of April there was a peak that reached down a value of about 78% but lasted only two days and the following values stabilized immediately again around 90% to 100% in winter (Fig. 8).



**Figure 8:** Sea ice concentration values in the cells over the MA and MB sites during 2008

### 3.6 Discussion

At both sites analyzed there is a high seasonal variability of mass and biogenic vertical fluxes mainly due to the coverage of ice that normally begins in late February and ends in mid-December. The trend of biogenic elements is similar to that of the mass flux, whose variations are so prevalent than those of the individual components. In particular, maximum fluxes are concentrated in late austral summer.

Although in the technical reports do not result an abnormal operation of the sediment trap, the mass flux measured in April for the MB is particularly high ( $609 \text{ mg}/(\text{m}^2\text{d})$ ), especially if we compare it with the period immediately before and after (when the flux are  $144 \text{ mg}/(\text{m}^2\text{d})$  and  $0.09 \text{ mg}/(\text{m}^2\text{d})$  respectively). We think that a temporary stop of the trap rotation occurred so the April bottle could

have collected even the particles of the following month. This high mass flux peak consequently has led to an high peak of carbon flux that probably has to be halved.

Moreover, in general, fluxes into the bottom trap are never zero in these areas, even during winter when the sea surface is almost completely covered by ice. This is due to bottom currents that play a fundamental role in the resuspension of particles and cause the trap to collect the material even during periods when primary productivity is absent (Frignani et al., 2000).

Looking at the mooring B mass flux trend (Fig. 3) we can observe that from mid-June to January the fluxes are unusually low. Moreover the values of biogenic silica fluxes are close to zero in June and in January; this is unusual because in this area the percentage of silica turn out to be rather high even during winter (Ravaioli et al., 1999; Langone et al., 2000).

Also at mooring A (Fig. 2) we observe from September low values in the mass and silica fluxes at the bottom level.

The integrated fluxes values (Table 5) and the fluxes time series (Figs. 2, 3) related to the two sites underline the differences between the two areas of the Ross Sea. The fluxes at mooring A are greater than those at mooring B, in fact mooring A is located in an area of the Ross Sea characterized by higher primary productivity than the mooring B area.

The fluxes values of biogenic silica obtained at mooring B are particularly low considering that the Joides Basin is an area characterized by high rates of silica accumulation.

Also the sample composition is affected by a high seasonal variability at both sites (Figs. 4, 5) with high values of carbonates during June 2008 and January-February 2009 (MB) and from June to mid-November 2009 (MA) and less than 50% of organic matter and biogenic material in almost all the samples. The high values of carbonates at site B coincide with the presence of a great amount of foraminifera (March-April 2008 and January-February 2009) and *Limacina helicina* (first fortnight of June) in the samples.

It is worth mentioning that in 2008 the sea ice has expanded more than the seasonal average and that the Ross Sea was, during the entire summer, surrounded by ice (Fig. 9). This could have affected the diatoms bloom and therefore justify the very low values of silica found at both sites.

The comparison between the MB 2008 annual integrated mass fluxes with the MB 1995 ones (Langone et al., 2000) evidence that during 2008 lateral advection processes were lower than during 1995 (Table 6).

**Table 6:** Annual integrated fluxes at site B in 2008 and 1995. (\* total fluxes on 697 days; \*\*discontinuous time series)

Site	Integrated mass flux (g/(m <sup>2</sup> yr))	Integrated C flux (g/(m <sup>2</sup> yr))	Integrated bio Si flux (g/(m <sup>2</sup> yr))	Integrated N flux (g/(m <sup>2</sup> yr))
MB 2008 top	11.6*	0.4*	0.5*	0.06*
MB 2008 bottom	22.8	3.4	2.8**	0.6
MB 1995 top	3.93	0.35	1.9	0.06
MB 1995 bottom	30.0	1.44	11.5	0.25

Comparing MA 2008 particle fluxes with those related to 1994 (Langone et al., 2003) we can observe (Table 7) that during 2008 fluxes were lower and the top trap collected more material than the bottom trap while in 1994 mass and bio-silica fluxes were higher at the bottom trap. We already



observed that usually during winter, when sea ice cover is total, fluxes are low at the top trap but not near seabed due to lateral advection and resuspension processes. Inter-annual fluxes variability is well known and our hypothesis is that the main responsible of such reduced fluxes is the sea ice distribution and concentration and consequently a lower and different distribution of algal bloom and a lower hydrodynamics. In fact the greater sea ice extension and concentration that surrounded the Ross Sea during 2008 can have inhibited currents.

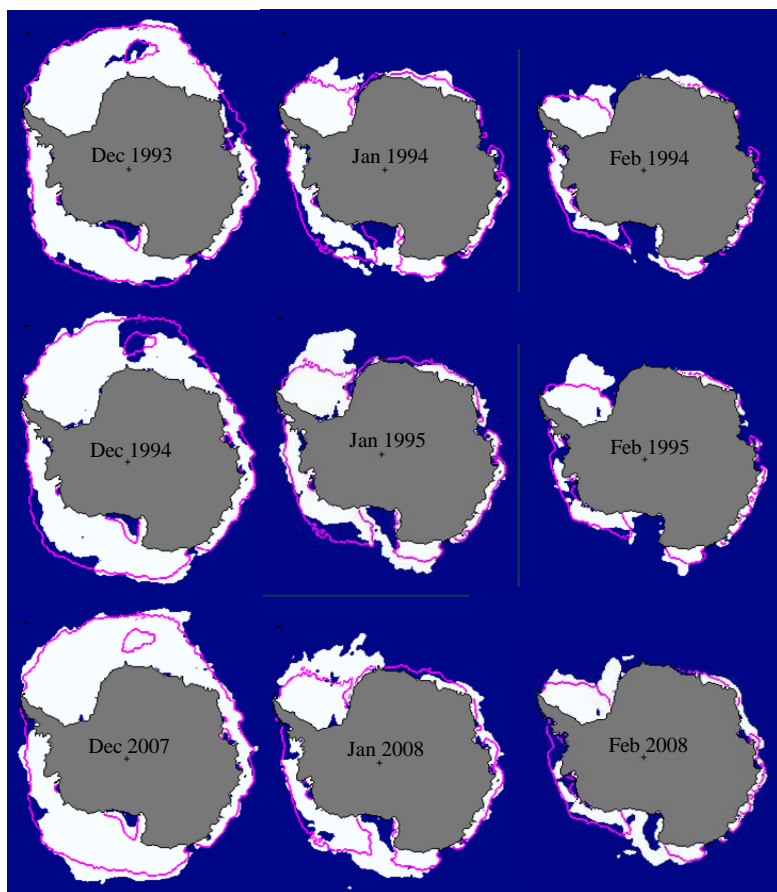
**Table 7:** Annual integrated fluxes at site A in 2008 and 1994

Site	Integrated mass flux (g/(m <sup>2</sup> yr))	Integrated C flux (g/(m <sup>2</sup> yr))	Integrated bio Si flux (g/(m <sup>2</sup> yr))	Integrated N flux (g/(m <sup>2</sup> yr))
MA 2008 top	47.8	3.8	10.8	0.6
MA 2008 bottom	36.1	2.5	9.1	0.4
MA 1994 top	59.3	10.6	26.3	--
MA 1994 bottom	86.9	4.1	52.4	--

If we consider the data of Antarctic sea ice extent during the years that we have compared (Table 8 and Fig. 9) we observe that in 2008 the values were significantly higher, while during 1994 and 1995 they were quite similar. For example, the Antarctic sea ice extent data related to December document a difference between the years 1993-1994 and 2008 approximately of 2,000,000 km<sup>2</sup>. Table 8 shows the average ice extent values during summer, period of maximum primary productivity. Moreover the average values in 2008 were higher than 1993 and 1994 throughout the year.

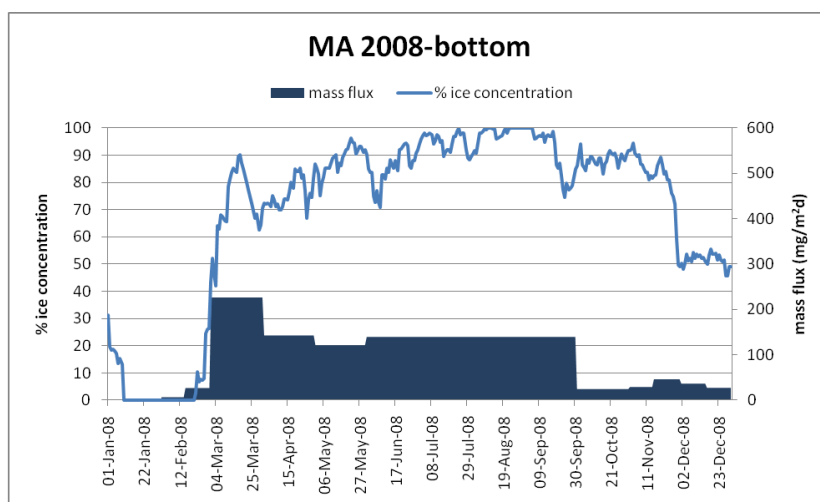
**Table 8:** Monthly average of antarctic sea ice during 1993-1994, 1994-1995, 2007-2008

Monthly average of Antarctic sea ice			
Years	December (million km <sup>2</sup> )	January (million km <sup>2</sup> )	February (million km <sup>2</sup> )
1993-1994	11.0	5.2	3.1
1994-1995	10.7	5.8	3.5
2007-2008	12.7	6.8	3.9



**Figure 9:** comparison between the ice cover related to 1994, 1995 and 2008 (data were provided by the EOS Distributed Active Archive Center (DAAC) at the National Snow and Ice Data Center, University of Colorado, Boulder).

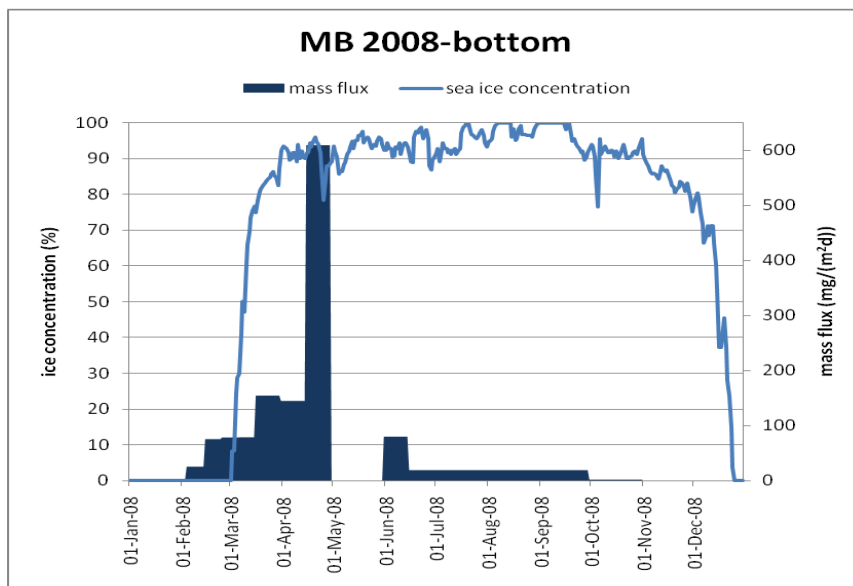
Figure 10 shows the daily sea ice concentrations on the grid cell above the mooring A compared with the mass flux at the bottom trap.



**Figure 10:** Mass flux trend at the mooring A bottom trap and daily sea ice concentrations during 2008

The peak of mass flux occurred immediately after the closure of the polynia and mass fluxes were never zero counting about 100 mg/(m<sup>2</sup>d) until the end of September.

Figure 11 shows the same parameters related to mooring B. At site B the maximum mass flux value occurred one month after the closure of the polynia and mass fluxes were negligible from June through December.



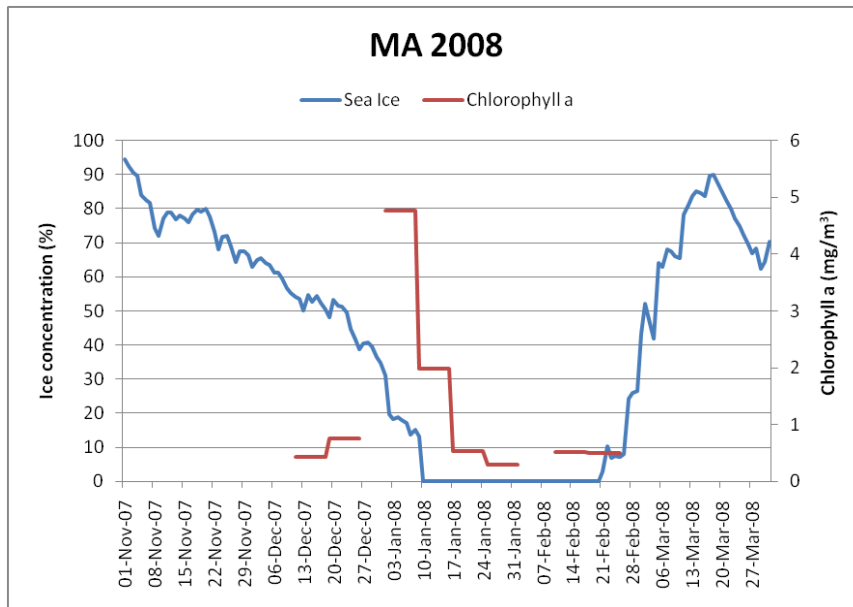
**Figure 11:** Mass flux trend at the mooring B bottom trap and daily sea ice concentrations during 2008

Fluctuations of the sea ice concentration at site A, compared with site B, were higher, reaching often values of 60-70% during winter, while the period of ice cover was about the same. Mooring A is located in a polynia area so the grid cell over this area is often partially ice free even during winter.

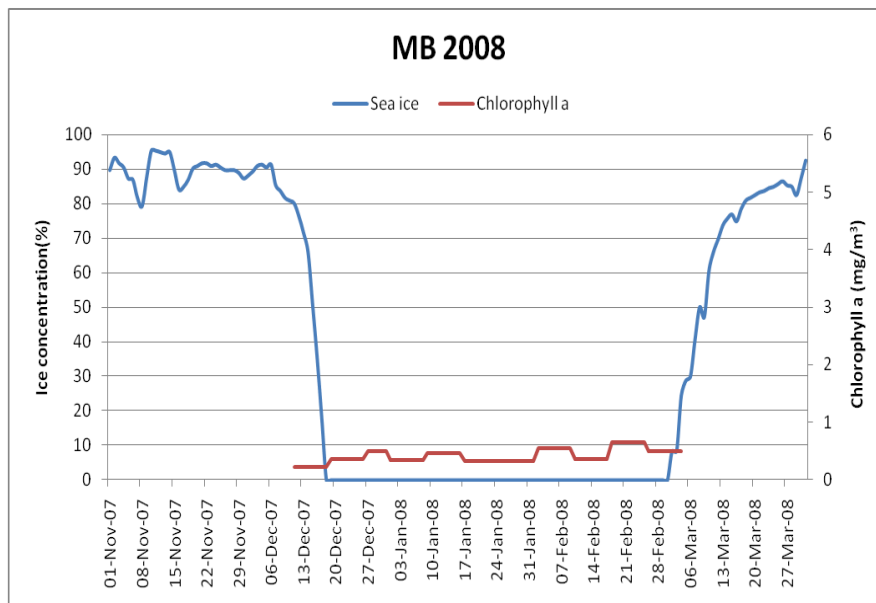
At both sites also organic carbon and biogenic silica fluxes high peaks occurred in March and April, when the ice cover begins to spread rapidly (from mid-February to mid-March there is the rapid extent of the ice) and its concentration reaches almost the maximum values (around 80-90% for site A and site B). The delay with respect to primary productivity maximum values, usually reached in these areas in late December or early January (Nelson et al., 1996; Smith et al., 2000), can be due to the lag between the phytoplankton growth and the development of zooplankton communities following the bloom of phytoplankton (Dunbar et al., 1998; Smith and Dunbar, 1998).

The maximum peak flux in the mooring A area happened at least one month before the one in the mooring B area. This is due to the phytoplankton bloom that occurred at site A in December and at site B in January (Fig. 14).

To better understand the low values of bio-silica measured at both sites, we processed the eight days chlorophyll a concentrations averaged in the two areas and we compared them with sea ice concentrations (Figs. 12, 13).



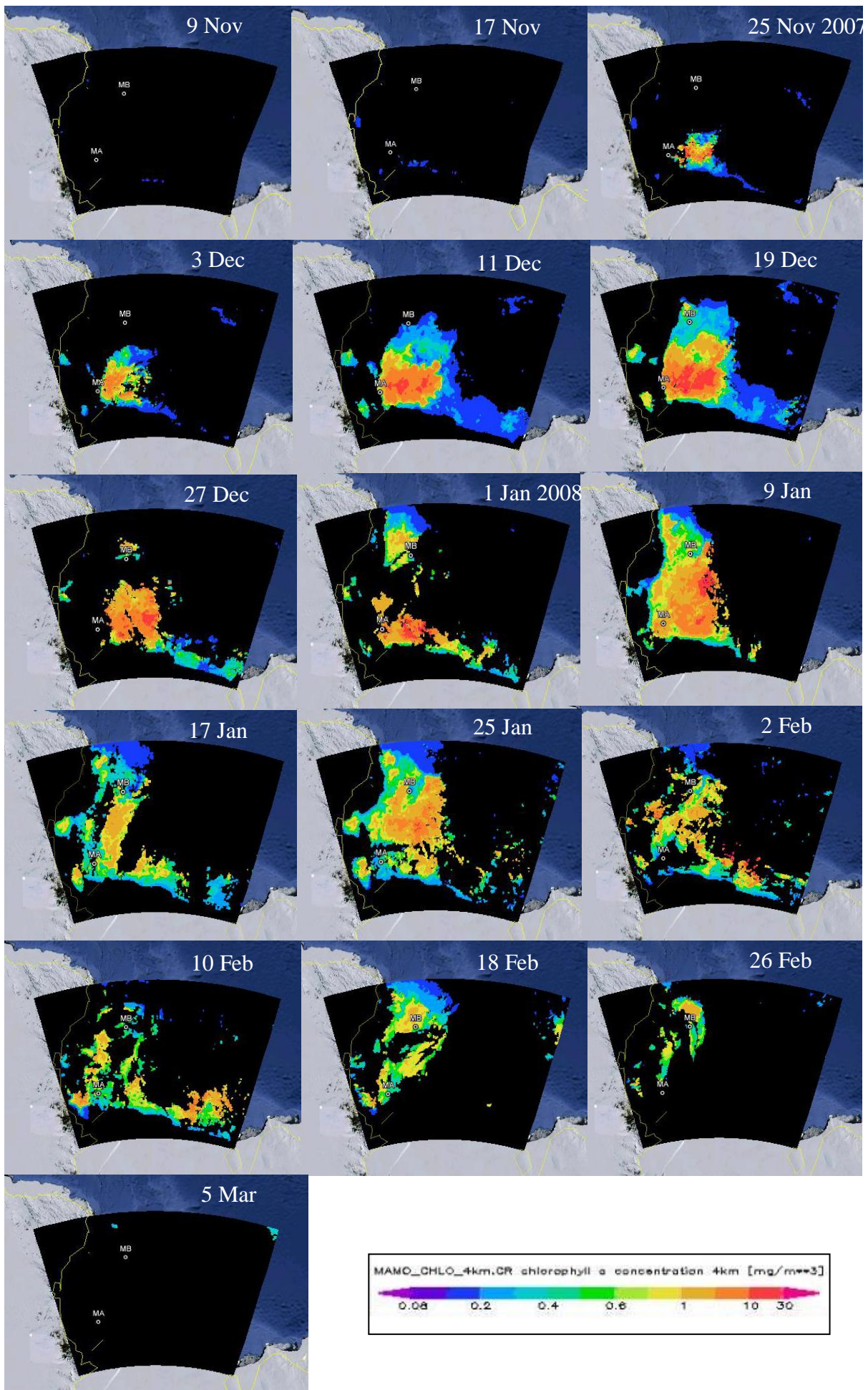
**Figure 12:** Chlorophyll a and sea ice concentrations at site A



**Figure 13:** Chlorophyll a and sea ice concentrations at site B

The chlorophyll a values at site A were quite high (from 2 to 5 mg/m<sup>3</sup>) during the first fortnight of January and low (under 0.5 mg/m<sup>3</sup>) in the last period ice free. At site B chlorophyll a concentration values remained always under 0.5 mg/m<sup>3</sup>. Since low values of chlorophyll a indicate poor primary productivity, this justifies the low flux values obtained meantime underlying the differences of the two areas in primary production.

Looking at a wider area of the Ross Sea (162.350°W, 72.00°S, 78.855°S, 162.670°E), we can observe that the values of chlorophyll a and its distribution may have affected the lateral advection processes usually present (Fig. 14).



**Figure 14:** eight days averaged chlorophyll a concentrations (data were derived from Moderate Resolution Imaging Spectroradiometer (MODIS) sensor on the Aqua satellite (4 km resolution) and provided by DAAC).



Since November, when the polynia area to the north of the Ross ice shelf is ice free, chlorophyll a values were fairly high with an average value around  $5 \text{ mg/m}^3$  and peaks of about  $30 \text{ mg/m}^3$  in a restricted area between  $170^\circ$  and  $177^\circ\text{E}$  and  $76^\circ$  and  $77^\circ\text{S}$  near mooring A, while the average value over the entire area was of  $1.65 \text{ mg/m}^3$ .

In December, the area affected by the bloom of phytoplankton greatly extended north to latitude  $73^\circ\text{S}$  and toward the south-east of the Ross Sea with an average of chlorophyll a concentration over the entire area of  $1.35 \text{ mg/m}^3$  and an extension of the area with the highest concentration of chlorophyll about three times greater than in November. In January the chlorophyll a concentration area extended but remained confined to the east of the antemeridian. In February, a bloom of phytoplankton developed in the west of the antemeridian while in the east the values of chlorophyll a were significantly decreased with average values over the area of  $0.9 \text{ mg/m}^3$ . Then there was a rapid decrease of the bloom in March, the extent of sea ice was maximum and chlorophyll a was quite zero (Fig. 14).

The surface currents in the southern Ross Sea are prevalently westward while along the western margin they are northward so it can be assumed a simplified clockwise circulation model for this area (Dunbar et al., 1998); then the chlorophyll a concentrations distribution mainly in the west of the antemeridian and values in general low may be the cause of the lack of fluxes during winter.

### 3.7 Conclusions

Our results document at both sites an high seasonal variability of biogenic and mass fluxes. The highest biogenic fluxes and total mass fluxes during 2008 are observed in March at site A and in April at site B, a few months after the seasonal bloom of phytoplankton, while fluxes are negligible from September-October through December.

Particle composition also presents a rather marked seasonal variability with unusually low fraction of organic matter and biogenic material and unusual high values of carbonates.

Furthermore, our results are in agreement with those obtained at the same sites in other years with regard to the trend, but not for the fluxes magnitude and the sample composition. The mass and biogenic fluxes values found are very much lower than those usually recorded especially at the bottom level in autumn and winter and consequently the sample composition is relatively poor in organic and biogenic material.

During 2008 the ice cover was larger if compared to previous years (1994 and 1995) and then the bloom of diatoms and the subsequent development of zooplankton may have been compromised. With the aid of satellite data it has been possible to relate sea ice and chlorophyll a concentration with our fluxes data justifying the values obtained with the high ice concentration and extent, the relatively low concentrations of chlorophyll a and its particular distribution.

Our results underline the different characteristics of the two areas considered: the annual fluxes at the mooring A area are higher and the maximum peak flux happens at least one month before the one at the mooring B area. The mooring A is in fact located in a polynia area that is first free from ice and therefore it is the area in which first the algal bloom develops.

Furthermore during this year we have not recorded important lateral advection processes at both sites due to the higher sea ice cover that we think has led to lower hydrodynamics and has inhibited algal blooms.

Sea ice extension and concentration has a complex relationship with atmospheric and oceanic parameters; each affects the other, so the connection between fluxes and sea ice actually involves climatic conditions.

## Acknowledgments

Sea Ice Concentration Data were provided by the EOS Distributed Active Archive Center (DAAC) at the National Snow and Ice Data Center, University of Colorado, Boulder, Colorado.

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## Chapter 4\*

### Time series data of biogenic fluxes in the Ross Sea (Antarctica): biogeochemical cycles and ENSO

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#### 4.1 Abstract

Biogenic and mass particle fluxes of trap samples, collected in the Joides Basin in north-western Ross Sea (Antarctica), were analyzed. The samples studied cover a period of time of 12 years. The mass flux annual integrated values related to 1999, 2005 and 2008 (respectively 42.48 g/(m<sup>2</sup>yr), 36.94 g/(m<sup>2</sup>yr) and 22.79 g/(m<sup>2</sup>yr) in the bottom trap) result in good agreement with the different concentration of sea ice. The data document a strong correlation between biogeochemical cycles and sea ice extent related to El Niño Southern Oscillation. In the western Ross Sea during El Niño years there is a decrease of temperature while during La Niña the situation is the opposite. In particular during 1996, 1998 and 1999 the sea ice concentration shows a direct correlation to El Niño Southern Oscillations (with an increase of sea ice during El Niño years) whereas during 2005 and 2008 a reverse correlation (with an increase of sea ice during La Niña years) is observed. Moreover, the maximum flux periods of particulate matter result different through the investigated years.

#### 4.2 Introduction

Many authors have investigated the relationship between sea ice advance and retreat and surface temperature anomalies in the Ross Sea (Southern Ocean) with El Niño Southern Oscillation (ENSO) phenomenon.

Van Woert et al. (2003) and Arrigo & Van Dijken (2004) correlate El Niño Southern Oscillation (ENSO) phenomena and particularly El Niño and La Niña periods with differences in the upper-ocean currents and in ice extension and concentration during the 1990s. Moreover it has been also observed that the relationship between ENSO and sea ice extension changes from one decade to another (Bertler et al., 2004). So, because ENSO phenomena changes over 8-10 years, it appears that changes in sea ice extension follow a cyclical pattern.

The Ross Sea is one of the regions with the highest primary productivity of the Southern Ocean (Comiso et al., 1993; Smith et al., 2006) so it represents an important site for the study of biogeochemical fluxes. These researches represent an important issue in monitoring climate changes linked to the different CO<sub>2</sub> exchanges between ocean and atmosphere (Takahashi et al., 2002).

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\* This chapter consists of a paper in preparation by Chiarini F., Capotondi L., Giglio F., Langone, L., Ravaioli, M., "Time series data of biogenic fluxes in the Ross Sea (Antarctica): biogeochemical cycles and ENSO" to be submitted to "Antarctic Science"

Previous studies (Dunbar et al., 1998; Langone et al., 2000) showed that mass and biogenic fluxes in the Ross Sea have a high seasonal and inter-annual variability highlighting the necessity to better investigate the links with primary productivity and climate factors. In order to obtain a global view of climate changes it is essential to have robust datasets from different areas.

With the aim of estimating changes in biogeochemical fluxes of this area we analyze here data from one mooring deployed in the northern part of the Joides Basin, a region characterized by low primary productivity, high biogenic silica deposits and great processes of resuspension and lateral advection (Langone et al., 2000) that can have a high influence in particle displacing (Jaeger et al., 1996).

The mooring allows to obtain data from the entire water column and to evaluate the influence of lateral advection of material. In this paper mooring B biogenic fluxes values related to trap samples collected over 13 years (1995, 1996, 1998, 1999, 2005, 2008) have been compared to explain factors that may influence the inter-annual variability.

### **4.3 Study area**

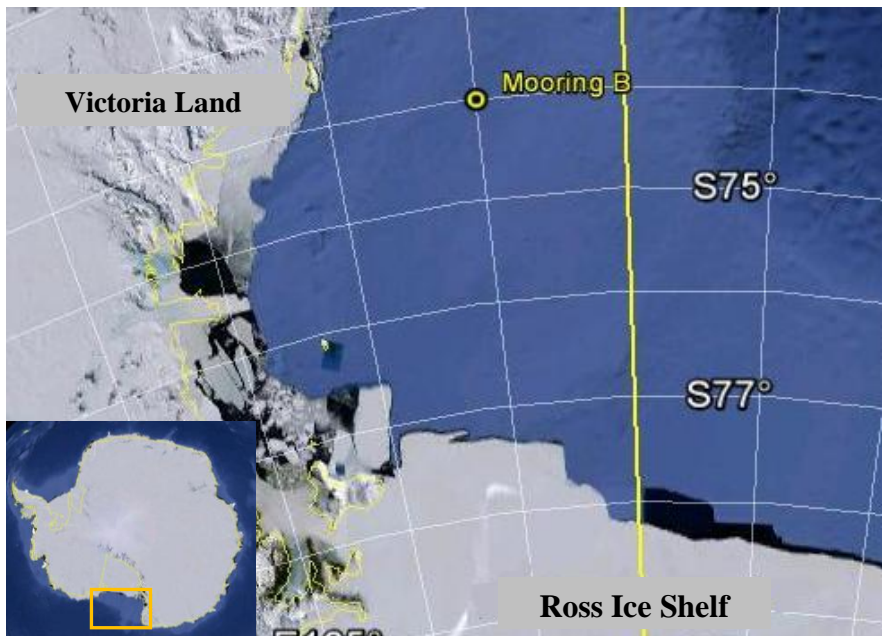
The continental shelf of the Ross Sea is characterized by basins that focus sediments from the neighbor banks, and the presence of polynia along the Ross Ice Shelf and the Terra Nova Bay coasts (Arrigo et al., 1998). The Ross Sea is rich in nutrients and characterized by vernal spatially widespread algal blooms during the ice retreat period (Smith and Nelson, 1985; Nelson and Smith, 1986).

As part of different projects, some moorings were deployed in areas considered strategic, because representative of particular conditions, with the aim of studying particles fluxes towards deep sea sediments, sedimentation processes, the cycle of biogenic particles and resuspension and lateral advection phenomena.

The site B is a survey site, active since 1994, located in the Joides Basin at 74°01'S and 175°05'E (Fig. 1). The water depth in this area is about 600 m and the length of the mooring is about 400 m. The study of this mooring is part of the Italian projects ROSS-MIZE, BIOSESO I and II, ABIOCLEAR and VECTOR.

The Joides Basin, located in the western Ross Sea, has a NE-SW direction and fine sediments are focused at its center from adjacent banks (Labbrozzi et al., 1998; Ravaioli et al., 1999).

This site is characterized by the intrusion of the Circumpolar Deep Water (CDW), the phytoplankton bloom is dominated by diatoms (siliceous algae) (Nelson et al., 1996) and so there is a substantial contribution to the sedimentation due to organisms with silica shell.



**Figure 1:** Study area and Mooring B location

Furthermore, in the Ross Sea cyclical variations related to El Niño-Southern Oscillation (ENSO) have been observed (Bertler et al., 2004; Stammerjohn et al., 2008). During years subjected to La Niña the effect consists in a decrease of surface waters temperature, during El Niño years the effects, however, are two: direct and indirect. The direct effect consists in an increase of the surface waters temperature and then, consequently, in a reduction of the ice extension. The indirect effect, however, causes a displacement towards the east of the  $L_{AS}$  (Amundsen Sea Low) which, in turn, increases the katabatic winds that blow from the continent. This causes a lowering of temperatures and thus an increase of the ice cover. The Amundsen Sea Low is a low pressure cell which usually stands in front of the Amundsen Sea (Bertler et al., 2006).

Even if these effects are opposite and they occur simultaneously, the indirect effect has a power of an order of magnitude larger than the direct effect and so they do not balance each other. The result is that the visible effects are only those due to the indirect effect, and therefore a greater extent of ice during the year subjected to El Niño (Bertler et al., 2006).

In the Ross Sea, however, both effects are present not in the entire area: in the east acts only the direct effect while in the west both. This causes a decoupling between what happens in the east and in the west. In the mooring B area both the direct and indirect effects of ENSO are present as it is located in the western Ross Sea (Bertler et al., 2006).

To measure the ENSO effects it is usually used the SOI (Southern Oscillation Index) which is the normalization of differences in surface pressure between Tahiti and Darwin. Positive values represent La Niña periods and negative El Niño (Parker, 1983). Previous studies (Bertler et al., 2004) showed a reverse correlation about every ten years between the temperature scale and this index in the Marie Byrd Land. Specifically, analyzing the data from 1970 to 2000, it was seen that for decades 1971-1980 and 1991-2000 the correlation temperature-SOI was positive while from 1981 to 1990 it was negative. The reasons for this alternation have not yet been explained but a hypothesis is that it is connected to cooling events on the continent (Bertler et al., 2006).

#### 4.4 Materials and methods

Here we report data determined at site B during the years 1996, 1998, 1999, 2005 and 2008. Concerning the year 1995 we used data provided by Langone et al. (2000).

Every year the mooring had a different arrangement although it usually consists of two instrumentation levels comprising a conical McLane sediment trap with a trap mouth of 0.5 m<sup>2</sup>, a current meter and a CTD (Table 1).

**Table 1:** Mooring B structure during 1996, 1998, 1999, 2005 and 2008

Year	Tool level	Sediment trap	Current meter	CTD
1996	top	219 m	227 m	228 m
	bottom	575 m	583 m	584 m
1998	top	257 m	279 m	278 m
	bottom	546 m	556 m	555 m
1999	top	264 m	285 m	286 m
	bottom	563 m	562 m	563 m
2005	top	----	220 m	----
	bottom	530 m	540 m	----
2008	top	243 m	245 m	243 m
	bottom	538 m	543 m	538 m

The top level of tools allows to measure the characteristics of particles flux exported from the euphotic zone. The bottom level allows to estimate the contribution of lateral advection and resuspension processes.

Sediment trap sampling intervals were synchronous between top and bottom traps except for 1996 and ranged from 7 days to about 3 months. Due to mechanical failures the predetermined number of samples has not always been collected. The number of samples and the sampling periods were different for every year with the sampling start ranging between January 1 and February 3 (Table 2). The instruments have worked quite well, except for some interruptions in traps rotation and in the current meters data acquisition. Due to current meters failures in 1998 and 2005 in the bottom level and at both levels in 2008, but with a reduction of only a few days, the data acquisition was not complete.

Due to mechanical failure the top trap of mooring B in 1999 did not finish bottles rotation but stopped at the seventh (late April), in 2008 the top trap collected the entire sediment into a single bottle.

**Table 2:** Number of samples and sampling periods of the Sediment Trap through the years

Year	Start	Stop	top samples (n°)	bottom samples (n°)
1996	26 Jan 1996	16 Dec 1997	11	3
1998	1 Jan 1998	13 Jan 1999	18	18
1999	23 Jan 1999	15 Jan 2000	7	18
2005	30 Jan 2005	28 Jan 2006	----	13
2008	3 Feb 2008	1 Feb 2010	----	21

Trap samples were examined at the time of recovery for a first estimation of mass fluxes, then transported to the ISMAR-CNR of Bologna and stored in a cold room. The samples of 1996, 1998 and 1999 were prepared for analysis using the Heussner method (Heussner et al., 1990), while those of 2005 and 2008 with the Heussner method modified (Chiarini et al., submitted; Chapter 2) here briefly described.

First of all we have removed part of the supernatant to preserve it. Then we have filtered the sample with a 580 microns mesh to sort out the coarse sediment from the finest.

Before proceeding with the splitting, we have removed the larger size swimmers by the way microscopical observation, then we have splitted the sample with a precision peristaltic pump to obtain three different fractions of material, one of which is held as an archive, one is kept wet and another is freeze-dried.

An accurate picking has been carried out under a stereomicroscope on the fraction of sample to be dried. The samples obtained were used for biogenic silica, carbon and nitrogen analysis.

The variants applied to the Heussner method do not affect the comparison between the values obtained. The swimmers removal, performed using a stereomicroscope on the two wet fractions obtained, has allowed to classify the organisms according to “South Atlantic Zooplankton” (ed. D. Boltovskoy, 1999). The different morphotypes of *Neogloboquadrina pachyderma* (sinistral) were identified according to Bergami et al. (2009). Subsampling was carried out using a high precision peristaltic pump.

The content of biogenic silica was obtained by the dissolution method suggested by DeMaster (1981). The total content of nitrogen and organic carbon were determined using a CHN analyzer. We used the following relations to evaluate the composition of the particulate matter:

$$\% \text{CaCO}_3 = (\% \text{C}_{\text{tot}} - \% \text{C}_{\text{org}}) * 8.33$$

$$\% \text{lithogenics} = 100 - (\% \text{C}_{\text{org}} * 2) - \% \text{CaCO}_3 - \% \text{BioSi} - \% \text{N}_{\text{tot}}$$

Sea ice concentration, which is the percentage of ocean covered by sea ice, was derived from the final daily data made available by the National Snow and Ice Data Center, obtained with the DMSP-F17 Special Sensor Microwave Imager/Sounder (SSMIS). This sensor has a resolution of 25 X 25 km<sup>2</sup> and the ice concentrations data represent a daily average on the grid cell. This data are generated using the NASA Team algorithm. The stereographic projection used a projection plane at 70 degrees southern latitude. The planar grid so obtained has the nominal resolution at 70 degrees and present a maximum distortion of 22 percent.

Chlorophyll a concentrations were derived from Moderate Resolution Imaging Spectroradiometer (MODIS) sensor on the Aqua satellite (4 km resolution) and from Sea-viewing Wide Field-of-view Sensor (SeaWiFS). Data were processed using the Giovanni online data system, developed and maintained by the NASA GES DISC.

To compare Chlorophyll a and ice concentration we have considered the smallest area that contains the grid cell used by the National Snow and Ice Data Center (Lat. 73.88°S-74.14°S, Lon. 175.01°E-175.92°E).

Diatoms concentrations are available online due to Goddard Earth Science Data and Information Services Center (GES DISC). Data were processed using the Giovanni online data system and are part of the NASA Ocean Biogeochemical Model (NOBM) which treats data from SeaWiFS and

MODIS. Diatoms concentrations were evaluated on the same area used for Chlorophyll a concentration.

## 4.5 Results

### 4.5.1 Particle fluxes

Mass and biogenic fluxes show inter-annual variability and organic carbon and bio-Si fluxes trend follows the total mass flux one through all years (Figs. 2, 3).

#### Year 1996

Integrated mass flux at the top trap was  $9.12 \text{ g}/(\text{m}^2\text{yr})$  while at the bottom trap data acquired does not allow to evaluate annual flux because the trap collected particles only for about one month. The highest mass flux was of  $162.74 \text{ mg}/(\text{m}^2\text{d})$ , value reached during February and the first half of March (Table 3).

Organic carbon fluxes ranged from  $0.05$  to  $14.08 \text{ mg}/(\text{m}^2\text{d})$ , biogenic silica fluxes ranged from  $0.03$  to  $87.88 \text{ mg}/(\text{m}^2\text{d})$  and nitrogen concentrations ranged from  $0.01$  to  $2.21 \text{ mg}/(\text{m}^2\text{d})$  (Table 4). The annual mean of C/N molar ratio was  $6.76$  and the mean of  $\text{SiO}_2/\text{OC}$  molar ratio was  $0.30$ .

#### Year 1998

In 1998 the data acquisition was complete at the two levels with an annual average value of mass fluxes of  $14.75 \text{ g}/(\text{m}^2\text{yr})$  at the surface and  $39.07 \text{ g}/(\text{m}^2\text{yr})$  at the bottom. The highest mass fluxes were reached at both levels in February with peak values of  $196.96$  and  $377.38 \text{ mg}/(\text{m}^2\text{d})$  respectively at the top and at the bottom trap (Table 3).

Organic carbon fluxes ranged from  $0.70$  to  $22.0 \text{ mg}/(\text{m}^2\text{d})$  at the top trap and from  $0.77$  to  $19.31 \text{ mg}/(\text{m}^2\text{d})$  at the low level. Biogenic silica fluxes varied from  $0.30$  to  $134.16 \text{ mg}/(\text{m}^2\text{d})$  at the top level and from  $1.98$  to  $226.22 \text{ mg}/(\text{m}^2\text{d})$  at the bottom trap. The range of nitrogen fluxes value was  $0.10$ - $1.94 \text{ mg}/(\text{m}^2\text{d})$  at the top and  $0.13$ - $2.58 \text{ mg}/(\text{m}^2\text{d})$  at the bottom (Table 4).

The annual mean of C/N molar ratio was about the same in both traps ( $6.94 - 6.96$ ) and the mean of  $\text{SiO}_2/\text{OC}$  molar ratio increased from  $0.88$  at the surface to  $3.00$  at the bottom.

#### Year 1999

In the surface trap the total mass integrated over 98 days was  $36.9 \text{ g}/\text{m}^2$  from February to May and it was  $42.48 \text{ g}/(\text{m}^2\text{yr})$  in the bottom trap during the entire year. Mass flux values were higher from February 15 to March 1 with a peak of  $807.58 \text{ mg}/(\text{m}^2\text{d})$  in the top trap and from March 1 to 16 with a maximum value of  $291.94 \text{ mg}/(\text{m}^2\text{d})$  in the bottom trap (Table 3).

The top trap presented mass flux highest values from February to March and a drastic decreasing from the second half of March. Unfortunately, we have samples of the top trap only until May. In

the bottom trap the mass flux remained quite high in the period from February 15 to April, we had another small increase in September and then fluxes started to rise again at the end of the year.

Organic carbon concentrations ranged from 3.0 to 13.7 mg/(m<sup>2</sup>d) in the top trap and from 2.0 to 6.6 mg/(m<sup>2</sup>d) in the bottom trap. Biogenic silica contents ranged from 10.37 to 319.4 mg/(m<sup>2</sup>d) in the top trap and from 5.35 to 149.45 mg/(m<sup>2</sup>d) in the bottom trap (Table 4). Nitrogen concentrations ranged from 0.69 to 5.78 mg/(m<sup>2</sup>d) at the top trap and from 0.27 to 1.76 mg/(m<sup>2</sup>d) at the bottom trap. The annual mean of C/N molar ratio was about the same in both traps (7.9 – 7.4) and the mean of SiO<sub>2</sub>/OC molar ratio increased from 1.83 at the surface to 2.71 at the bottom.

#### Year 2005

During 2005 MB was equipped only with one sediment trap near the bottom (Table 1).

The maximum mass flux was reached in the first half of February with a value of 313.17 mg/(m<sup>2</sup>d), while we found the minimum value of 24.75 mg/(m<sup>2</sup>d) during October (Table 3). The general trend of the flux was a bit different from usual because the values were high until May.

The integrated mass flux during the year was 36.96 g/(m<sup>2</sup>yr), the silica one was 8.93 g/(m<sup>2</sup>yr). Mass flux values ranged from 24.75 to 313.17 mg/(m<sup>2</sup>d), bio-silica fluxes ranged from 0.47 to 180.83 mg/(m<sup>2</sup>d) and organic carbon fluxes from 3.32 to 53.85 mg/(m<sup>2</sup>d) (Table 4). Nitrogen fluxes ranged from 0.63 to 10.79 mg/(m<sup>2</sup>d).

The annual mean of C/N molar ratio was 6.5 and the mean of SiO<sub>2</sub>/OC molar ratio was 0.51.

#### Year 2008

Only for the bottom trap it was counted the annual mass flux (22.79 g/(m<sup>2</sup>yr)) and the annual flux of silica (2.81 g/(m<sup>2</sup>yr)). In the bottom trap mass flux values were higher in March-April with a maximum of 609.22 mg/(m<sup>2</sup>d) and they decreased dramatically in May becoming quite null until September (Table 3).

The bio-silica fluxes ranged from 0 to 58.06 mg/(m<sup>2</sup>d) and showed a medium value of 0.74 mg/(m<sup>2</sup>d). Organic carbon ranged from 0.01 to 115.03 mg/(m<sup>2</sup>d) in the bottom trap and had a medium value of 0.57 mg/(m<sup>2</sup>d) for the entire year in the top trap (Table 4). Nitrogen fluxes ranged from 0 to 20.38 mg/(m<sup>2</sup>d) at the bottom trap and had a medium value of 0.09 mg/(m<sup>2</sup>d) in the top trap. The annual mean of C/N molar ratio was 7.8 at the top trap and 7.2 at the bottom; the mean of SiO<sub>2</sub>/OC molar ratio increased from 0.1 at the surface to 0.2 at the bottom.

In the bottom trap the highest values of organic carbon and biogenic silica occurred respectively in April and in March.

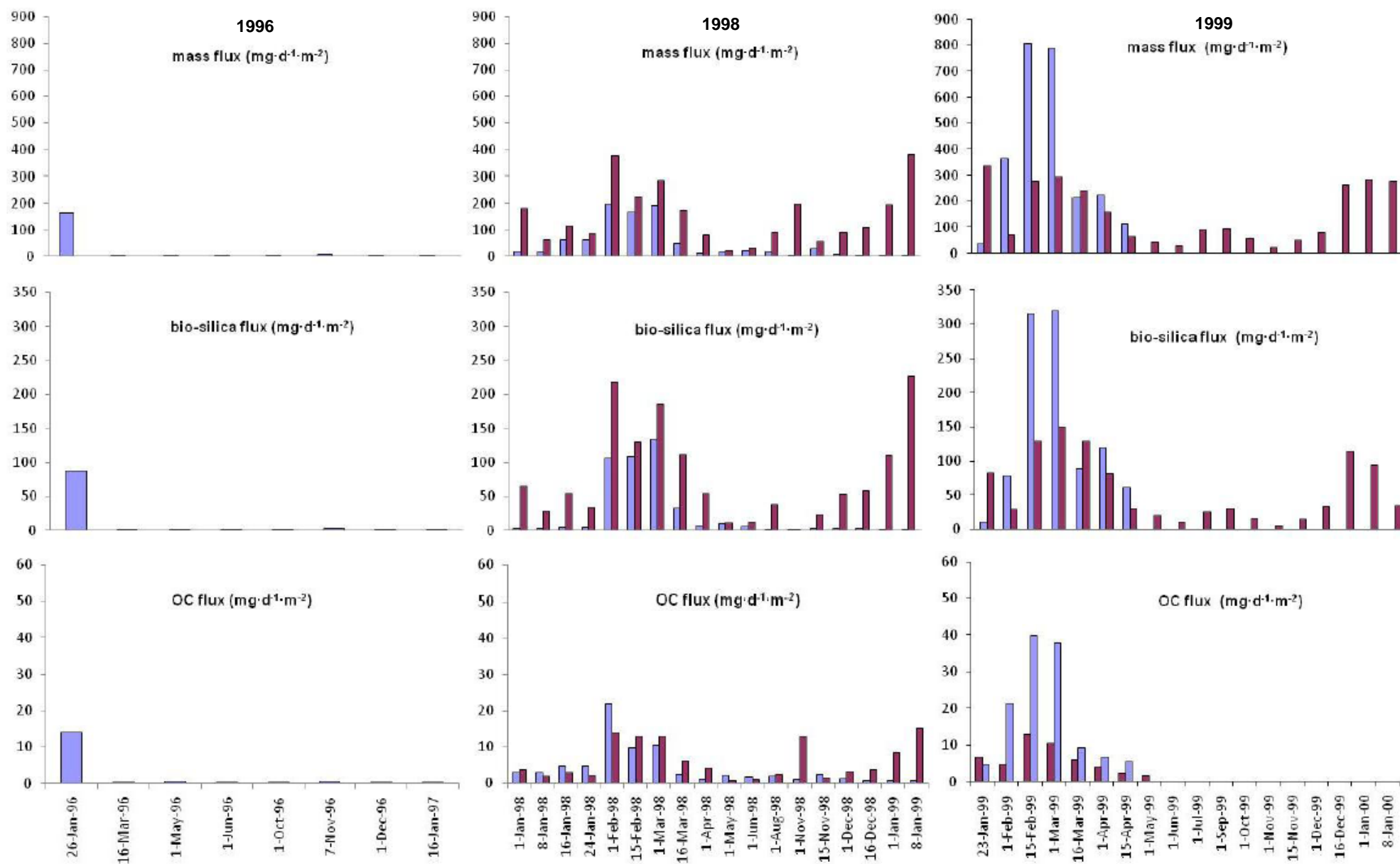


**Table 3:** maximum and minimum values of mass fluxes and sampling time interval

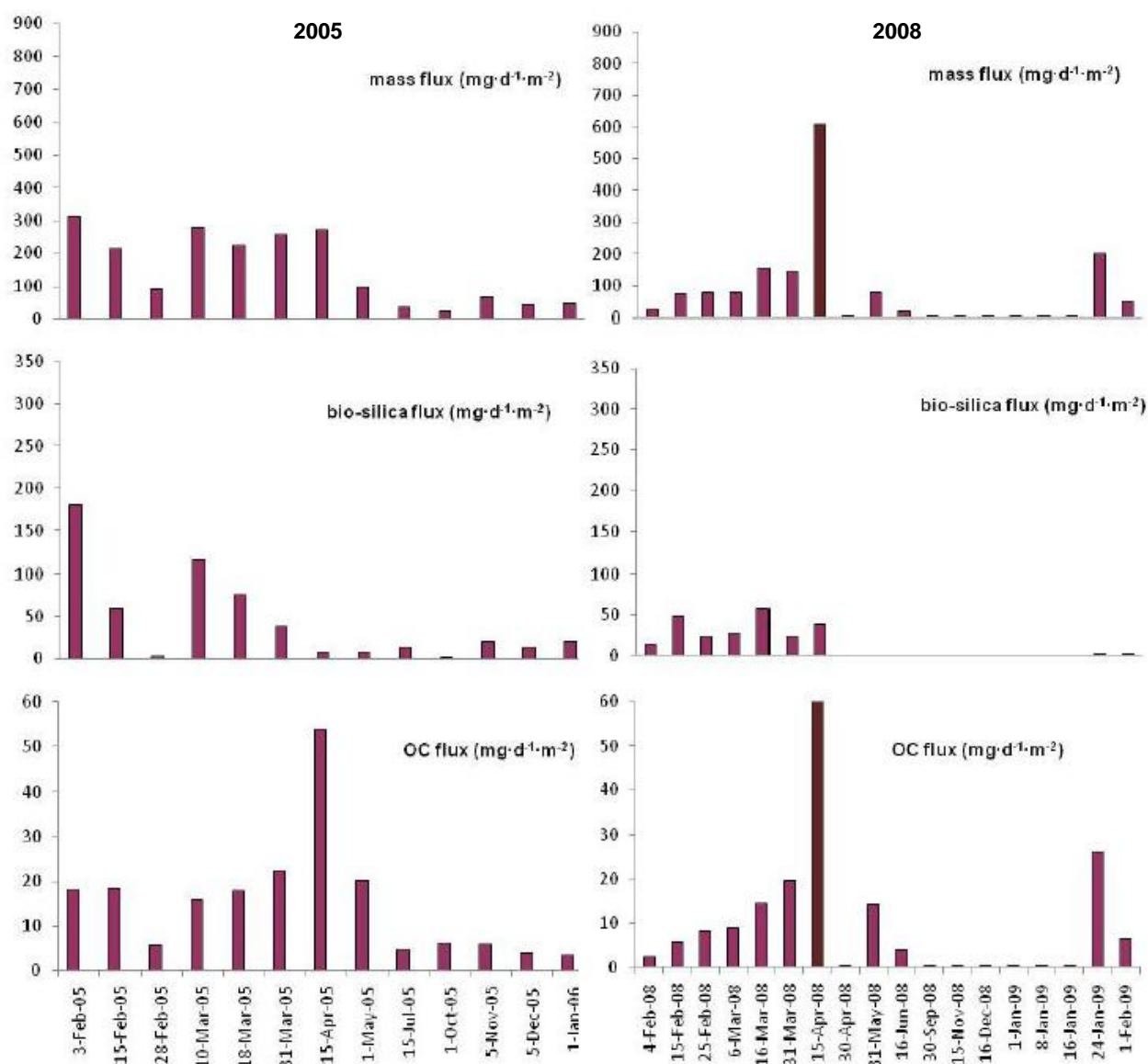
<b>Year</b>	<b>Top Mass flux (mg/(m<sup>2</sup>d))</b>	<b>Time interval</b>	<b>Bottom Mass flux (mg/(m<sup>2</sup>d))</b>	<b>Time interval</b>
<b>1996</b>	Max: 162.74	1/26-3/16	Max: 136.91	1/26-2/5
	Min: 0.79	6/1-10/1	Min: 12.96	2/5-2/15
<b>1998</b>	Max: 196.96	2/1-2/15	Max: 377.38	2/1-2/15
	Min: 2.86	11/1-11/15	Min: 21.91	5/1-6/1
<b>1999</b>	Max: 807.58	2/15-3/1	Max: 291.94	3/1-3/16
	Min: 33.6	1/23-2/1	Min: 22.17	11/1-11/15
<b>2005</b>	---	---	Max: 313.17	2/3-2/15
	---	---	Min: 24.75	10/1-11/5
<b>2008</b>	---	---	Max: 609.22	4/15-4/30
	---	---	Min: 0.09	4/30-5/31

**Table 4:** maximum and minimum values of Bio-Si and OC fluxes

<b>Year</b>	<b>Top BioSi (mg/(m<sup>2</sup>d))</b>	<b>Top OC (mg/(m<sup>2</sup>d))</b>	<b>Bottom BioSi (mg/(m<sup>2</sup>d))</b>	<b>Bottom OC (mg/(m<sup>2</sup>d))</b>
<b>1996</b>	Max: 87.88	Max: 14.08	Max: 71.19	Max: 10.18
	Min: 0.03	Min: 0.05	Min: 5.19	Min: 1.27
<b>1998</b>	Max: 109.39	Max: 22	Max: 226.2	Max: 15.1
	Min: 0.29	Min: 0.7	Min: 1.98	Min: 0.66
<b>1999</b>	Max: 319.4	Max: 13.7	Max: 149.45	Max: 6.6
	Min: 10.37	Min: 3.0	Min: 5.35	Min: 2.0
<b>2005</b>	---	---	Max: 180.83	Max: 53.85
	---	---	Min: 0.47	Min: 3.32
<b>2008</b>	---	---	Max: 58.06	Max: 115.03
	---	---	Min: 0	Min: 0.01



**Figure 2:** mass and biogenic fluxes related to 1996, 1998 and 1999. Blue: top level; purple: bottom level.



**Figure 3:** mass and biogenic fluxes related to 2005 and 2008 at the bottom level.

#### 4.5.2 Particle composition

The samples composition shows significantly different characteristics in the different years and between surface and bottom samples. The 1998 samples showed a similar composition to the 1995 ones (Langone et al., 2000) with a predominance of biogenic silica, high seasonal composition variability in the top trap samples and closer values into the bottom trap with higher rates of lithogenic material. We have found low percentage of organic carbon in both traps.

The particulate composition at the bottom trap during 2005 and 2008 was substantially different from those of 1998 and 1995, with high values of carbonate and low values of bio-silica and lithogenic material. It also showed a high variability. During 1996 only three samples were collected in the bottom trap, not enough to establish an annual trend of the particulates, and the top trap samples presented high values of carbonates.

### 4.5.3 Swimmers

The swimmers were catalogued only for 1999, 2005 and 2008.

**Table 5:** number of the most abundant swimmers found in the bottom trap samples of 1999, 2005 and 2008

Year	Crustacea	Pteropoda	Polychaeta
1999	447	1207	169
2005	1200	33472	673
2008	60	34471	100

**1999:** in the top trap the more abundant organisms were pteropods of the species *Limacina helicina* which reached the 2475 specimens for sample during the first half of February. Next, in order of abundance, we found crustaceans, like amphipods and copepods, and polychaetes; foraminifera were few. The top trap stopped working after the seventh sample, and then we lost a significant period of sampling from May to the end of the year.

In the bottom trap the organisms content was low and characterized by *Limacina helicina* that showed a maximum of 250 specimens during the first half of April. Likewise, polychaetes and crustaceans were fewer (Table 5). On the contrary mucilaginous clusters were very abundant.

**2005:** *Limacina helicina* resulted the most abundant taxon especially from mid-February to October, and it never dropped below 1000 individuals per sample (Table 5).

The distributional pattern of crustaceans (amphipods, copepods and ostracods) and polychaetes showed maximum values from May to July when they reached respectively 86 and 138 specimens counted on 3/8 of sample.

The samples collected during this year contained also different species of foraminifera (Table 6).

**Table 6:** Foraminifera identified in the 2005 bottom trap samples

period	<i>Neogloquadrina pachyderma sin</i>	<i>Neogloquadrina pachyderma dex</i>	<i>N. pachy morph 4</i>	<i>Turborotalia quinqueloba</i>	<i>Globigerina bulloides</i>	shells/ fragment	Number of specimens t
02/03 - 02/15	---	---	---	---	---	---	---
02/15 - 02/28	20	1	---	---	---	---	21
02/28 - 03/10	19	2	2	2	---	---	25
03/10 - 03/18	7	---	2	2	---	---	11
03/18 - 03/31	51	---	9	6	3	3	69
03/31 - 04/15	32	---	4	1	10	2	47
04/15 - 05/01	22	6	---	---	---	1	28
05/01 - 07/15	56	8	---	---	---	21	64
07/15 - 10/01	102	25	---	4	---	1	131
10/01 - 11/05	---	---	---	---	---	---	---
11/05 - 12/05	---	---	---	---	---	---	---
12/05 - 01/01	---	---	---	---	---	---	---
01/01 - 01/28	---	---	---	---	---	---	---

The foraminifera are not considered "swimmers" and were left within the sample as they are part of the passive flux, in fact they do not swim but they are carried away by water currents.

**2008:** pteropods, belonging to the *Limacina helicina* species, were the most abundant organisms found in the samples with a maximum of 11400 exemplary in the sample that collected the flux during first two weeks of June, followed by various types of polychaeta and of crustaceans such as amphipods and copepods (Table 5).

In these samples we found some specimens of foraminifera (especially of the species *Neogloquadrina pachyderma sinistral*) mainly between March and April 2008, and between January and February of the following year.

With the exception of the high number of foraminifera found in April, the period of maximum flux of organisms was from June to September. In these samples we found some fecal pellets (most abundant in the months of increased flux of organisms) with different shapes and colours.

#### 4.5.4 Sea ice cover

Sea ice in this area begin to form usually around March and melt during December (Dunbar et al., 1998). The extent and concentration of sea ice are related to climatic factors and therefore they vary on inter-annual scale. In 1996, the area was completely ice-free from January until March 20, when the ice began to form, and the concentration has increased to 90% in just 15 days. Sea ice formation is a very fast process and it usually ends in a maximum of 30 days (Dunbar et al., 1998). From April 5 to November 16, the ice cover has remained fairly constant to higher values with an average of 89.5%, maximum 98.8% and minimum of 71.2%. From November 16 the area was gradually ice free and within 15 days the concentration was back to 0 until the end of the year (Fig. 4a).

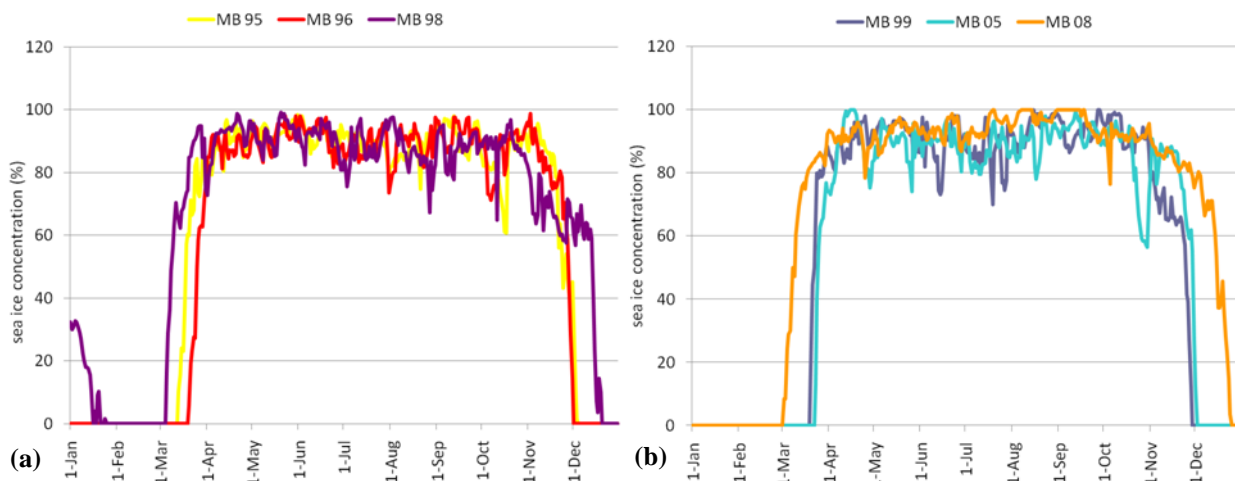
In 1998, the area was partially covered by ice since the beginning of the year until January 21, in open sea conditions until March 5 and within 20 days the concentration increased to 90%. From March 24 to November 16, there have been average and maximum values of the ice concentration similar to those of 1996 (89.4% and 99.2% respectively), but more variability with the lowest value of 64.8%. From December 1 to the end of the year the area remained ice free (Fig. 4a).

In 1999, the area remained ice-free for 79 days from the beginning of the year, the ice began to form on March 21 and on April 9 it has reached over 90%. From this period the concentration ranged from 70% to 100%, with an average of 91.5% until November 3, when the ice began to melt until the area was completely clear at the end of November (Fig. 4b).

In 2005, the ice free interval was similar to that of 1999. From April 8 the ice concentration remained between 80-100% until November 21 with an average of 88.8%. Towards the end of the coverage period ice concentration became more variable with a lower value of 56.4%. (Fig. 4b).

In 2008, the period of maximum ice extension lasted longer (from March 31 until December 3) with little fluctuations, an average value of 92.7% and a range from 75.2% to 100%. The ice formation began earlier than in other years (March 2) and the total melt was completed much later (December

24). Moreover in this year the ice extent was greater and more persistent with respect to the other years under review (Fig. 4b).

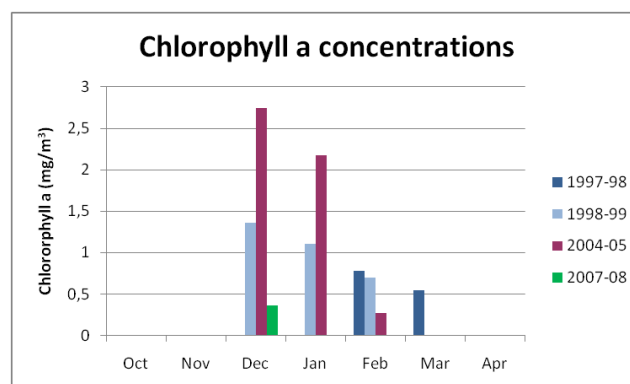


**Figure 4:** Sea ice daily concentrations at mooring B during (a) 1995, 1996, 1998 and (b) 1999, 2005, 2008.

#### 4.5.5 Chlorophyll a and diatoms

Data about chlorophyll a concentration are available from 1997, those of diatoms from 1998 until 31 December 2007 so it is not possible to compare the 1996 particles fluxes with both and the 1998 and 2008 ones with diatoms concentration.

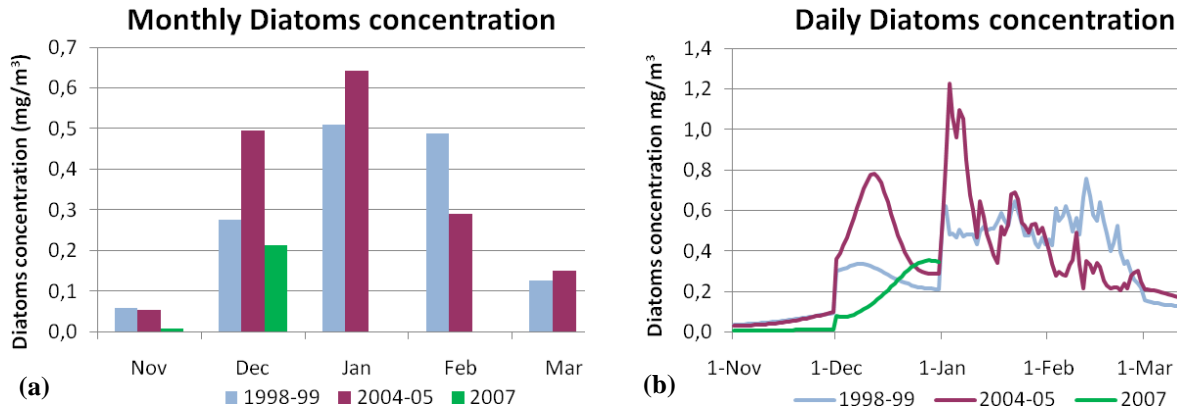
We have examined chlorophyll a concentrations data from November to April, period of higher primary productivity. The data show higher concentrations in 2004/05 with monthly average in December and January higher than  $2 \text{ mg/m}^3$ , in 1998/99 average concentrations were around  $1 \text{ mg/m}^3$  during the same period, and values less than 1 in 1997/98 and 2007/08 (Fig. 5).



**Figure 5:** Chlorophyll a monthly concentrations comparison

The diatoms concentration shows higher values for 2004/05, followed by 1998/99 and 2007/08, whose, however, no values are available from January 2008 (Fig. 6a).

In 1998-99, the concentration data of diatoms remained fairly constant with values between  $0.4$  and  $0.6 \text{ mg/m}^3$  in January-February, with a peak close to  $0.8$  in mid-February.



**Figure 6:** Inter annual comparison of (a) monthly diatoms concentrations and (b) daily diatoms concentrations

In 2004/05 the values were higher with peaks in December and January, respectively, of almost 0.8 and 1.2 mg/m<sup>3</sup>. From mid-January to early February the values ranged between 0.3 and 0.6 mg/m<sup>3</sup> in February and then they became lower than those of 1998/99 (Fig. 6b).

## 4.6 Discussion

### 4.6.1 Seasonal variability

The mass and biogenic fluxes show a high seasonal variability every year (Figs. 1, 2). Mass fluxes values range from zero to 162.74 or 807.58 mg/(m<sup>2</sup>d) in the top trap, depending on the years, and to 136.91 or 609.22 mg/(m<sup>2</sup>d) in the bottom trap. Bio-silica fluxes range from zero to 87.88 or 319.4 mg/(m<sup>2</sup>d) in the top trap and to 58.06 or 226.2 mg/(m<sup>2</sup>d) in the bottom trap.

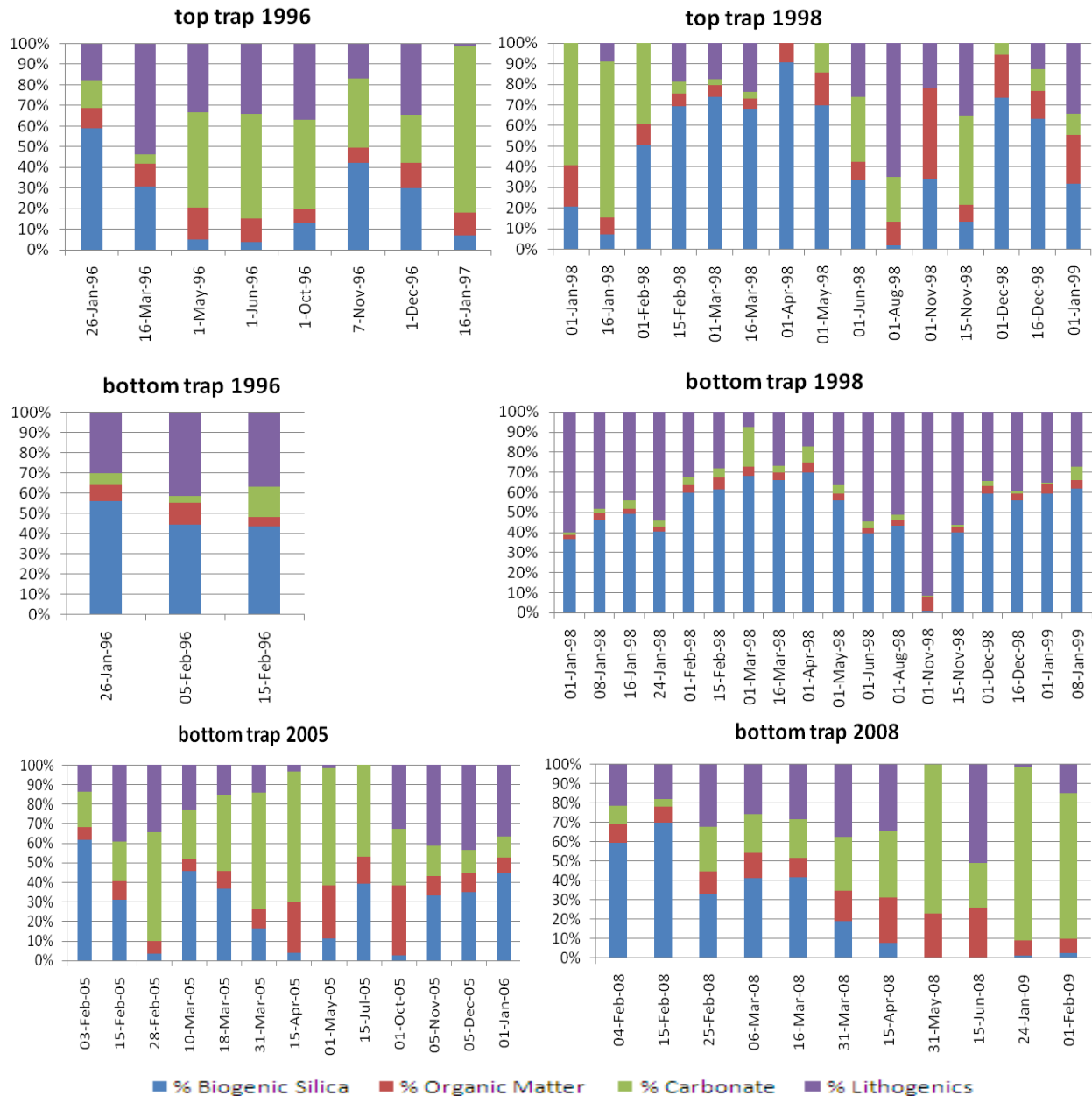
The greater amount of material at both depths is mainly collected during the austral summer; every years, at least 50% of the annual flux was collected from January to April with higher percentages in the surface trap (Figs. 2, 3). This is because the material collected at the top level is due almost exclusively to the particle vertical sinking, whereas at the bottom resuspension and lateral advection processes from neighboring areas are also present. So the bottom trap collects material even during periods of complete sea ice cover and the fluxes are not focused only in the first three months of the year.

The data document that mass flux peaks occurred each year at the bottom level one or two months after the peak of chlorophyll a concentration. This delay, usually observed, is due to the grazing, the growth rate of the zooplankton and the sinking speed of the particulate material.

Similarly, the maximum fluxes and percentages of bio-silica followed of one or two months the maximum peaks of diatoms concentration.

The mass and biogenic fluxes at the bottom level were almost never zero even during periods of total ice cover (1998, 1999, 2005. Figs. 1, 2) suggesting that the investigated area is affected by resuspension and lateral advection processes; during winter primary productivity is absent and so the material collected at the low level is focused from the neighboring banks.

Our results evidence high variability of the biological and lithological components at both levels during 2005 and 2008 (Fig. 7). The 1998 near bottom trap sample composition, instead, showed less variability such as the 1995 ones (Langone et al., 2000).

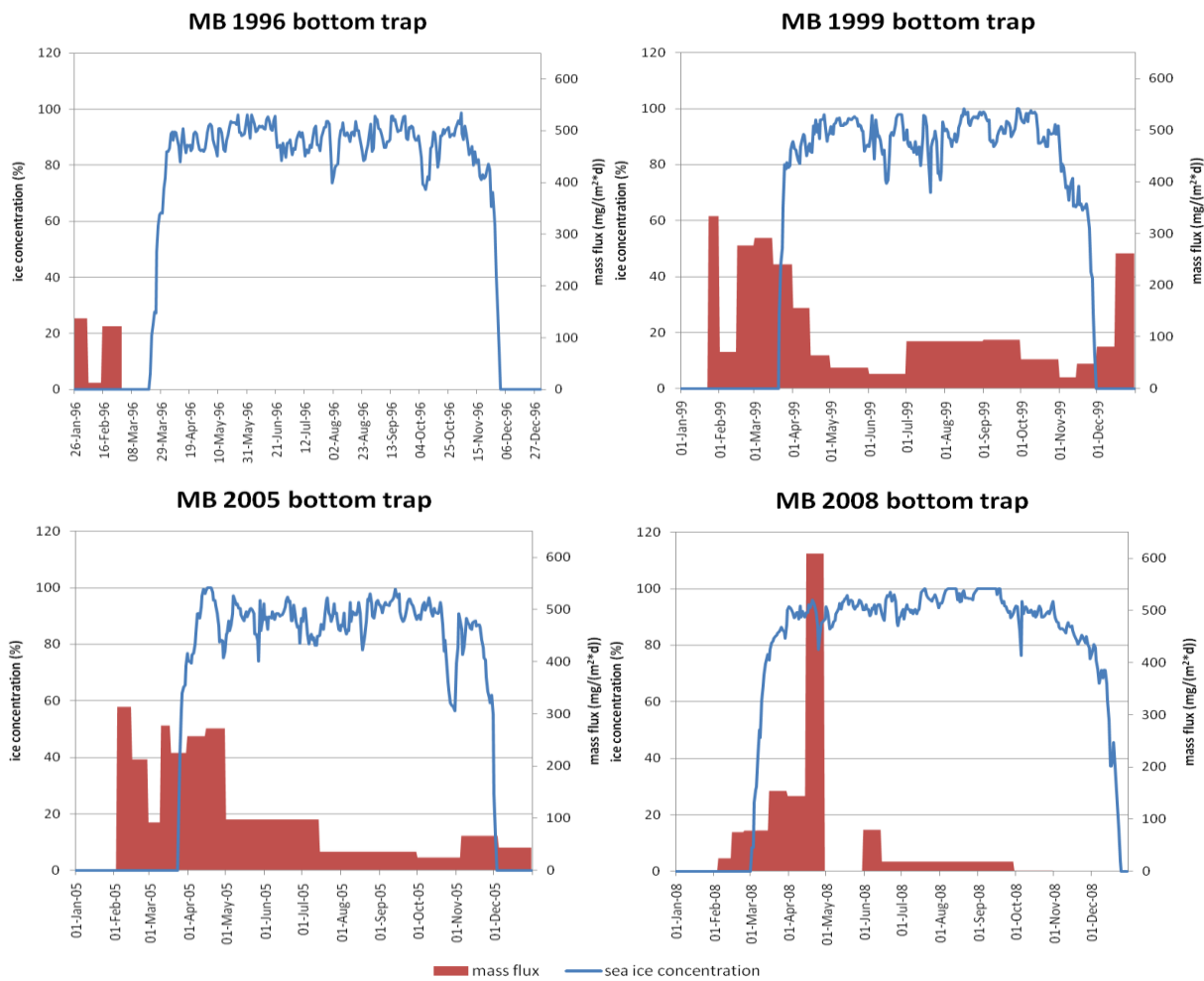


**Figure 7:** Sample composition at the top and bottom trap during 1996 and 1998 and at bottom trap during 2005 and 2008

#### 4.6.2 Inter-annual variability

The mass flux annual integrated values (Table 6) and their trend over time (Figs. 2, 3) show a high inter-annual variability. In fact in 1996 and 2008 there were rather low fluxes, while in 1998, 1999 and 2005 they were significantly higher. In 2008, the resuspension and lateral advection processes appear to have been negligible for several months (Fig. 3), unlike the other years.





**Figure 8:** Mass fluxes trend at the MB bottom trap during 1996, 1999, 2005 and 2008 and daily sea ice concentrations

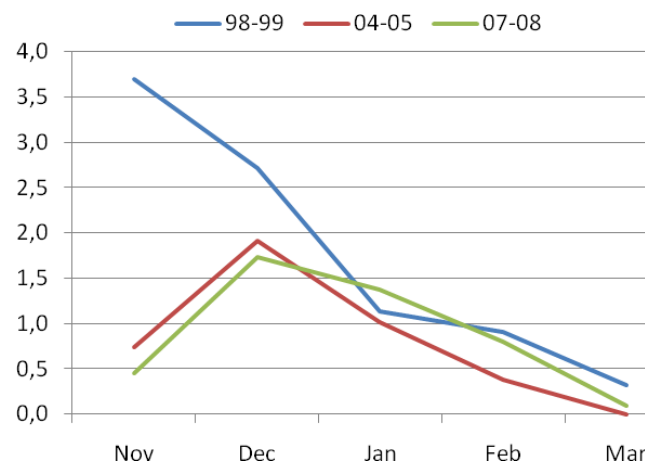
The area overlying the mooring B, in 2008, was longer covered by ice with concentration throughout the period around 90% (Fig. 8). This fact could have been decisive in inhibiting phytoplankton blooms. In 2008, moreover, the ice extent was greater than the seasonal average and the Ross Sea has never been completely sea ice free. During 1996, in spite of a 79 days ice free, mass and bio-silica fluxes were quite low (Fig. 8). Unfortunately chlorophyll a and diatoms concentration values are not available for this year but primary productivity in the Ross Sea is controlled by sea ice, irradiance, surface wind stress and nutrients (Dunbar et al., 1998). So, in this year, strong winds or waters depleted in nutrients could have affected algal blooms.

In 1999 and 2005 (Fig. 8), the study area remained longer ice-free in summer and concentrations showed greater fluctuations with average values lower than in 2008. During these two years chlorophyll a and diatoms concentration values were quite high, greater during 2005 than 1999 (Figs. 5, 6b). This appears in contrast with the integrated mass and bio-silica fluxes (Table 7) slightly greater in 1999 than in 2005. In the northwestern Ross Sea sediments are transported for many tens of kilometers, maybe even off the shelf (Frignani et al., 2000). For this reason sediments do not necessarily reflect the processes that happens along the water column. In fact, in this area,

during summer and autumn pulses of modified Circumpolar Deep Water may deliver particles from adjacent areas (Langone et al., 2000).

If we consider the chlorophyll a concentrations averaged on the entire Ross Sea (Fig. 9), they result higher during 1999 than in 2005. So the higher integrated fluxes during 1999 could be due to lateral advection processes.

In 1998 and 1999, the molar ratio between bio-silica and organic carbon has reached, at the bottom, values greater than 2, against the top values below 1 and 2 respectively, indicating a greater preservation of silica along the water column. In 2005 and 2008 these molar ratios are less than 1 and this is unusual because the site B is generally characterized by high accumulation of bio-silica.



**Figure 9:** Chlorophyll a concentrations averaged on the Ross Sea area

**Table 7:** Annual integrated values of mass and biogenic fluxes. (\*) integrated values over the first 98 days of sampling.

Year	Level	Mass g/(m <sup>2</sup> yr)	Bio Si g/(m <sup>2</sup> yr)	OC g/(m <sup>2</sup> yr)	N tot g/(m <sup>2</sup> yr)	CaCO <sub>3</sub> g/(m <sup>2</sup> yr)	Lithogenics g/(m <sup>2</sup> yr)
1996	top	9.12	4.68	0.79	0.13	1.26	1.59
	bottom	---	---	---	---	---	---
1998	top	14.75	6.60	1.18	0.20	3.08	2.56
	bottom	39.07	20.40	1.55	0.26	1.94	15.48
1999	top	36.87*	14.50*	0.02*	0.003*	---	---
	bottom	42.48	16.32	0.007*	0.001*	---	---
2005	bottom	36.94	8.93	4.62	0.83	12.22	5.21
2008	bottom	22.79	2.81	3.42	0.59	7.49	5.41

During 2008 we observe higher values of lithogenic material in comparison to the biogenic content. This fact is probably due to the longer duration and greater extent of sea ice in 2008, which also occurred in 1998. The particle composition in 1998 confirm this hypothesis, showing high lithogenics percent.

In 2005 the mass flux was quite high, with high values of silica and carbonates. High carbonates fluxes values are due to the presence of foraminifera and of many empty and broken shells of *Limacina helicina*. These organisms are also present in large quantities in 2008 samples.

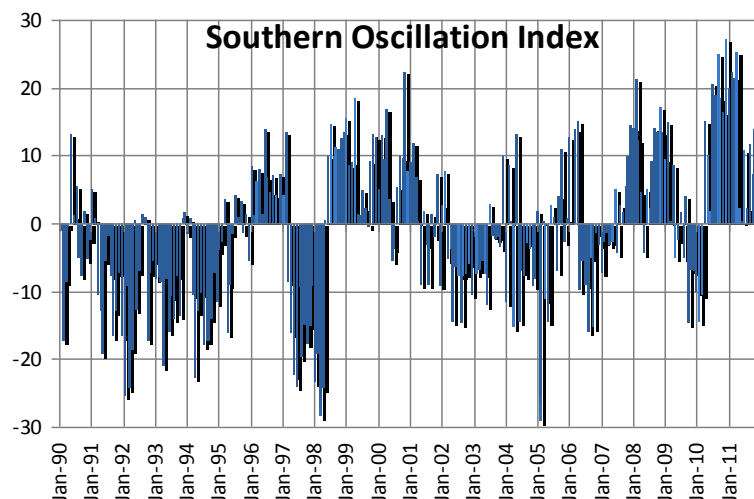
### 4.6.3 Sensitivity of Ross Sea to ENSO variability

The inter-annual variability of fluxes is related to different factors as well as the physical and chemical conditions of waters, the sea ice formation and melting processes and the climatic variations.

Sea ice data related to the mooring B area are in agreement with the atmospheric forcing in the 90's; sea ice concentrations were lower in 1996 and 1999 (La Niña periods), higher during 1998 (El Niño period) and intermediate in 1995 (transition El Niño – La Niña period). During 2005 the SOI shows positive and negative values denoting a transitional period, while in 2008 SOI positive values indicate a La Niña period (Fig. 10).

Van Woert et al. (2003) and Stammerjohn et al. (2008) showed a correlation between the atmospheric changes linked to ENSO variability and the physical parameters of waters in the Ross Sea. The changes due to ENSO on intensity and direction of currents, on winds and on temperatures affect the extent and concentration of sea ice and vice versa the sea ice extent and melting in turn affect the conditions of temperature, salinity and density of water.

The sea ice concentration values in 2008 does not match with positive SOI (La Niña) because they are as high as those of 1998 (El Niño). Bertler et al. (2004) showed opposite response to changes in ENSO in the 80's with respect to the 90's, this may indicate a change on decadal scale. Our 2000's data show an opposite response to the SOI with greater sea ice extent during La Niña periods. So the hypothesis is of a reverse correlation that occurs about every ten years between the temperature scale and the SOI in the western Ross Sea.



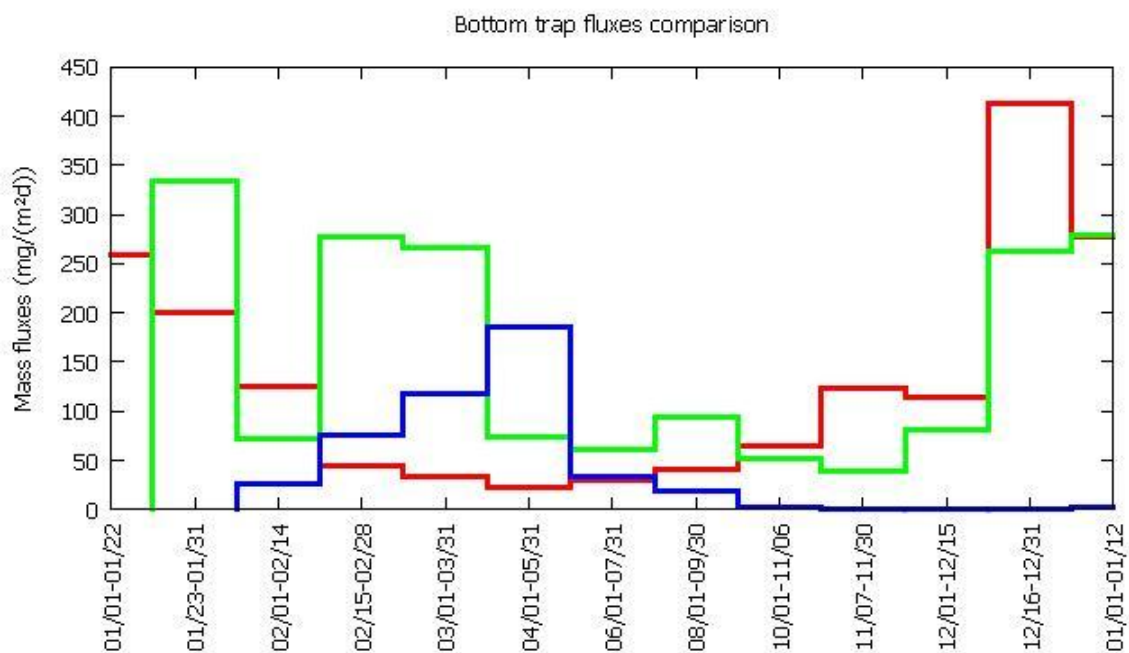
**Figure 10:** twenty years data of the Southern Oscillation Index. Negative SOI values lower than -8 often indicates El Niño episodes, SOI positive values greater than 8 are indicative of La Niña episodes. (data from Bureau of Meteorology - Australian government)

However, the changes in the processes of formation and melting of sea ice are not sufficient to justify the inter-annual variability of fluxes (Table 7). In fact our fluxes data are in agreement with these findings showing high values during 1999 (annual integrated mass flux of  $42.48 \text{ g/(m}^2\text{yr)}$ ), medium-high values during 2005 (annual integrated mass flux of  $36.94 \text{ g/(m}^2\text{yr)}$ ) and low values during 2008 (annual integrated mass flux of  $22.79 \text{ g/(m}^2\text{yr)}$ ). They disagree during 1996 whose

fluxes values are low, and during 1998 which shows high fluxes values (annual integrated mass flux of 39.07 g/(m<sup>2</sup>yr)) in despite of the presence of a great sea ice extent.

#### 4.6.4 Phytoplankton bloom inter-annual variability

Looking at the mooring B time series, it is then worth mentioning that the maximum peak of mass flux shows a forward displacement in the months. In 1995, in fact, the highest mass flux value occurred in January (Langone et al., 2000), in 1998 and 1999 between February and March and in 2005 and 2008 between March and April (Fig. 11)



**Figure 11:** Mass flux trends during 1995 (red line), 1999 (green line) and 2008 (blue line)

Usually the maximum export flux in the Ross Sea occurs at least two months after the peak of productivity that is usually in December or early January (Dunbar et al., 1998; Collier et al., 2000). The biomass produced is sequestered in the surface layer for a long time if compared to other high productivity ecosystems and this is mainly due to the difference between the development of the phytoplanktonic community and the zooplankton growth. If we compare the maximum monthly chlorophyll a and diatoms concentrations related to 1999 and 2005, averaged over the mooring B area (Figs. 5, 6), with the respective vertical mass and bio-silica fluxes (Figs. 2, 3), we observe that the highest fluxes during 1999 occurred about one month later the phytoplankton bloom while in 2005 they happened about two months later. But if we consider the chlorophyll a concentrations averaged over the Ross Sea area (Fig. 9) the highest values during 1999 occurred in November while in 2005 they occurred in January. Assuming the presence of focusing processes from

neighboring areas in which the algal bloom occurred in November the lag between the maximum of productivity and the highest fluxes has been for both years of about two months.

Usually in this area the particulate composition is dominated by the biogenic component, but significant differences can be highlighted in samples from different years (Fig. 7). During 1998 the biogenic component was predominant with high values of bio-silica at both levels. During 1996, 2005 and 2008 silica values were lower while the %CaCO<sub>3</sub> was predominant during 2005 and showed very high values in 2008 and 1996. These differences are well underlined by the SiO<sub>2</sub>/OC molar ratios. In 2005 and 2008 the mean molar ratio was respectively 0.5 and 0.2 while during 1998 and 1999 it was 3.0 and 2.7. Less than 1 SiO<sub>2</sub>/OC molar ratios are unusual in this area which is dominated by diatoms. During 2008 low values of bio-silica could have been due to the higher sea ice concentration and extension and consequently shorter and less intensive diatoms blooms. The low SiO<sub>2</sub>/OC molar ratio during 2005 is not due to low bio-silica values but to higher organic carbon values (Fig. 3).

In general, if the amount of lithogenic material is different between the top trap and the bottom trap it can be deduced the presence of processes of lateral advection, resuspension or removal in the area. These phenomena do not have the same intensity during the years since they are related to the intensity and direction of the currents, the extent of algal blooms, the processes of melting and formation of ice and, in general, to the physical and chemical conditions of the waters.

Unfortunately it was not possible to study the inter-annual variability of these processes in the mooring B area because only the 1998 complete series of values of top and bottom traps are available.

Observing the percentages composition of the 1998 samples we note that the amount of lithogenic material is greater in the bottom trap sediments than in the top ones. This fact confirms the hypothesis that this area is subjected to high lateral advection and resuspension processes (Langone et al., 2000).

In addition, by comparing the biogenic and mass fluxes between bottom and top we can observe that fluxes are greater at the bottom level. Obviously the major amount of material cannot be due to gravitative fall along the water column but it must have been transported by the currents from the surrounding areas. In fact, even without taking into account the dissolution processes, we could expect about the same amount of material found in the top trap. The deep circulation in the mooring B area is eastward and then the sediment is probably focused from the Mawson Bank (Langone et al., 2000).

During 2005 the sediment traps have collected the largest number of organisms. This agrees with the lower sea ice concentrations recorded during this year compared to the other ones. Mass and biogenic fluxes were indeed in general higher and the high fluxes lasted longer (e.g. in 2005 the mass flux was high from March to May while during the other years this range was of a couple of months).

Very poor organisms (a few crustaceans and polychaetes) have been found in 2008 trap samples except for *Limacina helicina*. This is probably due to limited algal blooms and consequently low rate of zooplankton growth.

During 2005 and 2008 many specimen of *Limacina helicina* have been found in the bottom trap samples, about one order of magnitude greater than in 1999. Many of them were intact and so they

have been removed as swimmers. Collier et al. (2000) assumed that high numbers of this species, even if intact, have to be considered part of passive flux if in other samples of the same year or in samples from nearby areas there is the same abundance. This assumption is based on the fact that it is unlikely that at the same time in different traps many specimen of *Limacina helicina* have entered alive. In our case it was not possible to verify this correspondence because we do not have data about samples of both levels and of other sites. So when the pteropods were found with shell and intact organs we classified them as swimmers.

#### 4.7 Conclusions

We analyzed biogenic transfer from the surface to the sea floor using time-series traps deployed in the Ross Sea from 1996 to 2008. Our results show a high seasonal and inter-annual particle fluxes variability. This paper investigates the causes of this variability taking into account the mass and biogenic fluxes, the extent and concentration of the sea ice, the concentration of chlorophyll a and diatoms and the interactions between atmospheric events (ENSO) and sea ice concentrations.

We observe that particle fluxes reach the highest values one or two months after the phytoplankton bloom and are negligible during winter, when the sea ice cover is total.

The inter-annual variability is highlighted by the differences in average annual fluxes, changes in maximum peak of export and the different composition of the material collected into the traps. The flux values during 1999, 2005 and 2008 are in a good agreement with the different concentration of the sea ice, which in turn appears to be related to the response of the high latitudes atmosphere to the fluctuations of ENSO.

The similar conditions of sea ice concentrations observed in 1998 and 2008 as in 1995 and 2005 suggest the occurrence of a cyclical pattern over ten years.

Our data show low concentrations of sea ice during La Niña periods (1996 and 1999) and high sea ice concentrations during El Niño periods (1998). This correlation seems to be denied if we look at the data related to the years of the next decade. In fact 2008, which has the greatest concentration of sea ice, is subjected to a La Niña year. This suggest a reverse correlation that occurs about every ten years in the western Ross Sea between the SOI and the sea ice formation and melting processes.

Finally the analysis of fluxes time series data highlights a shift towards the autumn months of maximum peaks of mass flux and consequently of the biogenic ones. Even if the data we have collected cover a 13 years period it is not possible to establish whether this is a cyclical trend or an actual movement linked to climate changes.

Actually we need more investigations in order to understand the climatic cyclicity observed in this region.

## **Acknowledgments**

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We thank Dr. M. Ligi for the assistance in the revision of the program used to extract sea ice data.

Sea Ice Concentration Data were provided by the EOS Distributed Active Archive Center (DAAC) at the National Snow and Ice Data Center, University of Colorado, Boulder, Colorado.

Chlorophyll a and Diatoms concentrations analyses and visualizations used in this paper were produced with the Giovanni online data system, developed and maintained by the NASA GES DISC.

Southern Oscillation Index data were provided by the Bureau of Meteorology - Australian government.

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## Chapter 5\*

### Sediment trap particle fluxes during two years (2005 and 2008) in the Ross Sea polynia (site A)

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#### 5.1 Abstract

In this paper we present data about biogenic and mass particle fluxes of trap samples collected in the Ross polynia area, in the south-western Ross Sea (Antarctica). The samples were collected during 2005 and 2008 at site A (76°41'S - 169°02'E), managed jointly by United States and Italy.

The mass flux annual integrated values related to 2005 and 2008 were respectively 42.2 g/(m<sup>2</sup>yr) and 47.8 g/(m<sup>2</sup>yr) at the top trap and 102.7 g/(m<sup>2</sup>yr) and 36.1 g/(m<sup>2</sup>yr) at the bottom trap. The highest mass fluxes occurred in February and March, about two months later the algal bloom.

Data document an high inter-annual variability in fluxes magnitude, in samples percentage composition and in lateral advection processes due to differences in the development of algal blooms, in sea-ice extent and in water hydrodynamics.

The mass balance between top and bottom levels has highlighted the presence of lateral advection processes only during 2005 and the decoupling between bio-silica and organic carbon cycles.

#### 5.2 Introduction

The Ross Sea is one of the areas with the highest primary productivity of the entire Southern Ocean, and as such can contribute significantly to the CO<sub>2</sub> uptake from the atmosphere (Dunbar et al., 1998). It is therefore a unique area to carry out climate studies as changes in primary productivity throughout the year are tightly related to light availability, sea ice occurrence, physical and chemical parameters of the water column and the availability of dissolved nutrients that affect the development of phytoplankton blooms, zooplankton and, consequently, the carbon export (Frignani et al., 2000).

The study of particles collected by automatic sediment traps allows to estimate primary productivity and to link it with the parameters mentioned above.

In this study we examined sediment trap samples collected at two different depths (360, 770 m) during the years 2005 and 2008 from mooring A, located in the south-western Ross Sea, managed jointly by United States and Italy and we compare them with the results obtained by Langone et al. (2003) during 1994. As part of the ABIOCLEAR project, this research aims to determine dissolution, regeneration, transport and accumulation processes along the water column and to investigate the factors that control the regional, seasonal and inter-annual variability of one of the

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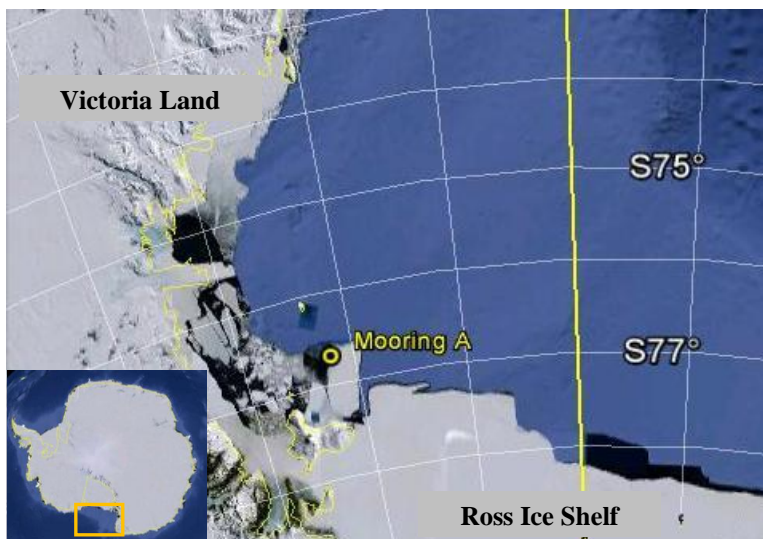
\* This chapter consists of a paper in preparation by Chiarini F., Capotondi L., Dunbar R.B., Giglio F., Langone, L., Ravaioli, M., Sangiorgi F., "Sediment trap particle fluxes during two years (2005 and 2008) in the Ross Sea polynia (site A)" to be submitted to Journal of Marine Systems.

most productive areas of the Southern Ocean. The Southern Ocean is one of the most important areas for the potential sequestration of CO<sub>2</sub> in the ocean and is expected to be vulnerable to changes in C export forced by anthropogenic climate change (Sarmiento et al., 1991). For this reason, understanding the biogeochemical processes occurring in the Southern Ocean and their relation with annual phytoplankton blooms in seasonal ice zone is fundamental to determine the contribution of the Southern Ocean to the CO<sub>2</sub> drawdown and its role in a changing climate (Frignani et al., 2000).

### 5.3 Study area

Mooring A is located in the south-western region of the Ross Sea polynia, between the Franklin Island and the Ross Island (Fig. 1). It is one of the more productive areas of the Ross Sea (Comiso et al., 1993; Sullivan et al., 1993; Arrigo et al., 1998) and for this reason it has represented an important site for particle flux studies along the entire water column since the 1990 year. From 1994 it has become a site to which Italy and USA cooperate.

The mooring A area is characterized by diatom blooms (Smith and Nelson, 1985) and, when ice melts, it borders the marginal ice zone for most of the austral summer (Ravaoli et al., 1999). Primary productivity is subjected to high seasonal and inter-annual variability (Smith et al., 2006). The inter-annual variability of the Ross Sea is also linked to changes in the currents that differ depending on the area (Frignani et al., 2000). In the south-west area, where mooring A is positioned, the currents are quite weak and allow the largest particles to sink in close proximity (< 20 km) of the production area. This means that high primary productivity usually determines a high accumulation of biogenic silica in the sediments nearby (Jaeger et al., 1996).



**Figure 1:** Position of Mooring A in the south-western Ross Sea

## 5.4 Materials and methods

Mooring A was deployed at 76°41'S latitude and 169°02'E longitude in 832 m water depth and it was equipped with two levels of instruments. The equipment position along the mooring did not differ much in the two years of study (2005, 2008) with surface sediment traps at 360 and 370 m and near bottom traps at 770 and 780 m, respectively. Each set of instruments was equipped with a RCM9 current meter, a SBE SeaCat conductivity and temperature recorder and a McLane sediment trap.

In 2005, sediment traps were equipped with 21 cups, while in 2008 each level contained 13 cups. The sediment traps have collected material between February 8, 2005 and January 16, 2006 and between February 1, 2008 and February 1, 2009.

Unfortunately, few bottles of the year 2005 broke during transport to the laboratory making the data set not complete. Moreover, the collected material in some samples was too scarce to be able to perform the analyses. 11 samples for the top level and 12 for the bottom trap could be analyzed and only 8 samples are related to the same period. On the contrary, in 2008, the time series of sediment trap sample was complete.

After recovery, trap samples were stored in a cold room at the ISMAR-CNR of Bologna. The 2005 samples were prepared for analyses at ISMAR-CNR of Bologna with the Heussner method modified (Chiarini et al., submitted) while the 2008 samples were splitted and analyzed at Stanford University. We have splitted the sample to obtain three different fractions of material, one of which is held as an archive, one is kept wet and another is freeze-dried. An accurate picking has been carried out under a stereomicroscope to remove the organisms that entered alive into the trap (active flux) and so obtain samples consisting of passive flux.

Dinoflagellate concentrations in the top trap of mooring A 2008 have been determined on the wet fraction as number of organisms/ml samples at the Utrecht University.

The biogenic silica content was obtained using the DeMaster (1981) dissolution method based on the different behavior in basic solution of the biogenic silica with respect to the mineral one, which have different dissolution rates.

The total nitrogen and organic carbon content was determined using a CHN analyzer. The following relations have been used to evaluate the composition of the particulate matter:

$$\begin{aligned}\% \text{CaCO}_3 &= (\% \text{C}_{\text{tot}} - \% \text{C}_{\text{org}}) * 8.33 \\ \% \text{lithogenics} &= 100 - (\% \text{C}_{\text{org}} * 2) - \% \text{CaCO}_3 - \% \text{BioSi} - \% \text{N}_{\text{tot}}.\end{aligned}$$

Sea ice concentrations have been derived from the daily data made available by the National Snow and Ice Data Center, obtained with the DMSP-F17 Special Sensor Microwave Imager/Sounder (SSMIS). The sensor resolution is a cell 25 X 25 km<sup>2</sup> wide and the sea ice concentrations data represents the daily values averaged on the grid cell containing site of the mooring A.

This data are based on the NASA Team algorithm and the stereographic projection uses a plane at 70 degrees southern latitude as projection plane. The planar grid so obtained has the nominal resolution at 70 degrees and present a maximum distortion of 22 percent. Sea ice concentration data have been processed starting from November 1993 to December 1994, from November 2004 to December 2005 and from November 2007 to December 2008.

Chlorophyll a concentrations (available from 1997) have been derived from Moderate Resolution Imaging Spectroradiometer (MODIS) sensor on the Aqua satellite (4 km resolution). Data were processed using the Giovanni online data system, developed and maintained by the NASA GES DISC. Chlorophyll a concentration data have been processed starting from November 2004 to February 2005 and from November 2007 to February 2008.

To compare chlorophyll a and sea ice concentration we have considered the smallest area containing the grid cell surrounding site A used by the National Snow and Ice Data Center. The chlorophyll a concentrations have been so averaged on the region 76.60°S-76.89°S latitude and 167.87°E-169.105°E longitude.

## 5.5 Results

### 5.5.1 Samples composition

Integrated annual mass fluxes during 2005 was 42.2 g/(m<sup>2</sup>yr) at the top trap and 102.7 g/(m<sup>2</sup>yr) at the bottom trap while during 2008 it was 47.8 g/(m<sup>2</sup>yr) in the surface level and 36.1 g/(m<sup>2</sup>yr) near the seabed. 2005 experimental data cover a time interval of 257 days at the top level and 229 days at the bottom one, while the 2008 data cover the entire year.

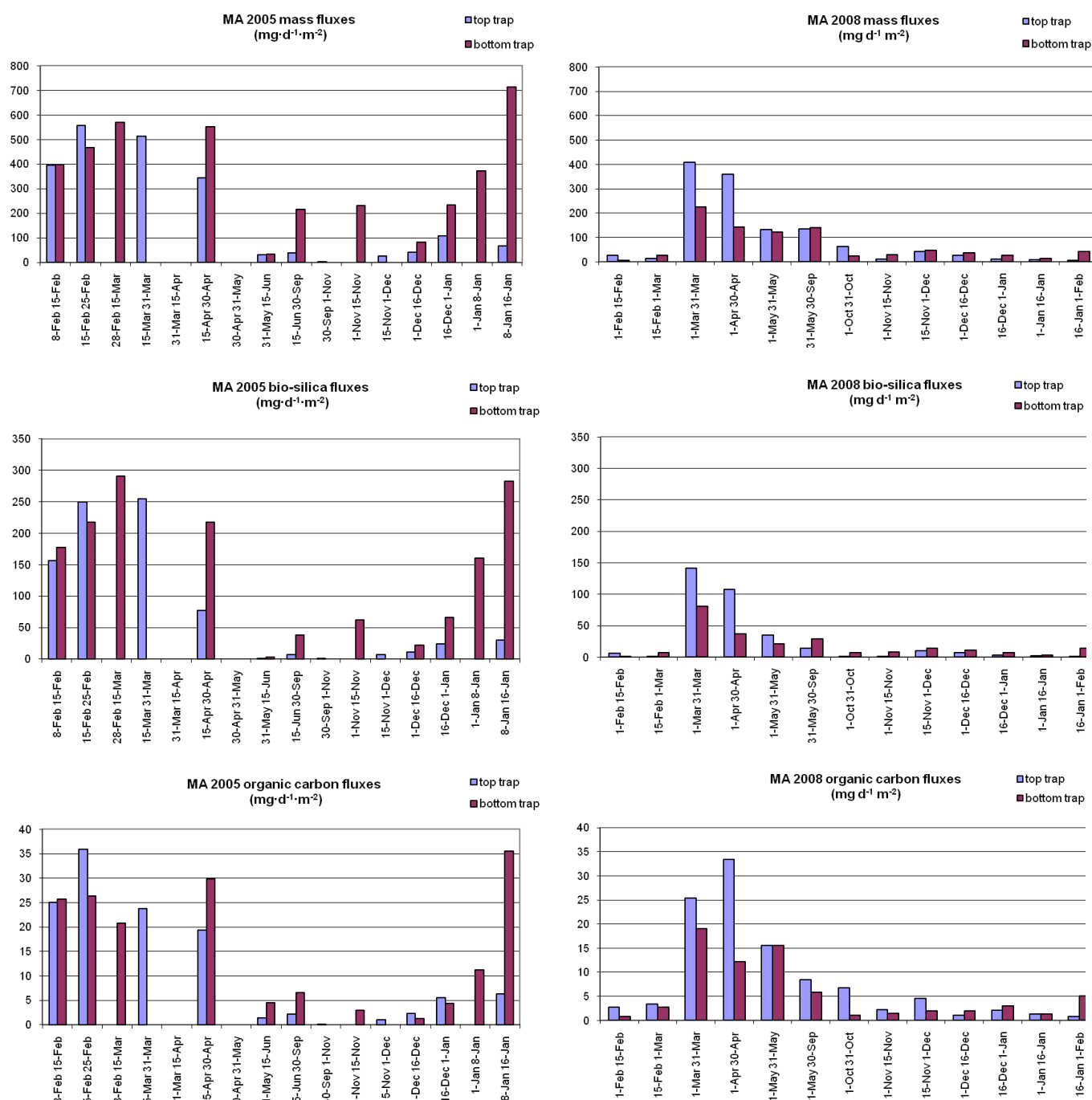
All biogenic fluxes follow the mass flux trend (Fig. 2). Furthermore they had lower values at the top than at the bottom during 2005 and they showed the opposite trend during 2008 (Table 1).

**Table 1:** Annual integrated particle fluxes during 2005 and 2008 at mooring A. 2005 fluxes are integrated over 257 days at the top and 229 days at the bottom.

Years	Level	Mass g/(m <sup>2</sup> yr)	Bio Si g/(m <sup>2</sup> yr)	OC g/(m <sup>2</sup> yr)	N tot g/(m <sup>2</sup> yr)	CaCO3 g/(m <sup>2</sup> yr)	Lithogenics g/(m <sup>2</sup> yr)	molar SiO <sub>2</sub> /OC
2005	top	42.2	15.0	2.3	0.4	7.6	16.0	1.0
	bottom	102.7	33.1	3.9	0.7	6.8	54.9	1.8
2008	top	47.8	10.8	3.8	0.6	20.1	12.3	0.4
	bottom	36.1	9.1	2.5	0.4	12.1	10.1	0.9

During 2005 mass fluxes ranged from 1.9 mg/(m<sup>2</sup>d) to 557.3 mg/(m<sup>2</sup>d) at the top trap and from 32.8 mg/(m<sup>2</sup>d) to 712.5 mg/(m<sup>2</sup>d) at the bottom trap. Biogenic Silica (Bio Si) content ranged from 0.3% to 49.3% at the top trap and from 9.2% to 50.9% at the bottom trap. Organic Carbon (OC) concentrations ranged from 1.0% to 6.4% at the top trap and from 1.3% to 13.5% at the bottom trap (Table 2). C/N molar ratio ranged from 6.0 to 8.7 at the top trap and from 6.3 to 7.5 at the bottom trap with almost the same mean value 7.0 and 7.2 respectively. SiO<sub>2</sub>/OC molar ratio showed different values at the two levels with a mean value of 1.0 at the top and 1.8 at the bottom.

For the year 2005, the highest mass fluxes were obtained from February through March at the top level while at the bottom level very high fluxes were observed also in April and the highest fluxes in the second week of January 2006. Bio-silica fluxes were about one order of magnitude higher than organic carbon fluxes and reached their maximum values on March at both levels (Fig. 2).



**Figure 2:** Mass, bio-silica and organic carbon fluxes at the top and bottom trap during 2005 (to the left ) and 2008 (to the right)

During 2008 mass flux values were slightly higher than in 2005 in the top trap and much lower in the bottom trap, ranging from 5.0 to 409.6  $\text{mg}/(\text{m}^2\text{d})$  at the top trap and from 6.0 to 226.1  $\text{mg}/(\text{m}^2\text{d})$  at the bottom trap. They were the highest during March at the two levels (Fig. 2).

**Table 2:** temporal series of mass, organic carbon and bio silica fluxes and of bio silica, organic carbon and nitrogen content related to mooring A 2005. (\*) anomalous values .

Sample	Start	Stop	Days	Total flux (mg/(m <sup>2</sup> d))	%C org	%SiO <sub>2</sub> biogenic	%N	C flux (mg/(m <sup>2</sup> d))	Si flux (mg/(m <sup>2</sup> d))
Top 1	2/8/2005	2/15/2005	7	395.1	6.3	39.5	1.2	25.0	156.1
Top 2	2/15/2005	2/25/2005	10	557.3	6.4	44.8	1.2	35.9	249.6
Top 5	3/15/2005	3/31/2005	16	514.2	4.6	49.5	0.8	23.7	254.5
Top 7	4/15/2005	4/30/2005	15	342.8	2.3	22.5	0.9	19.4	77.0
Top 9	5/31/2005	6/15/2005	15	30.2	4.7	0.3*	0.8	1.4	0.1
Top 10	6/15/2005	9/30/2005	107	39.6	2.0	18.7	0.9	2.2	7.4
Top 11	9/30/2005	11/1/2005	32	1.9	2.4	23.8	0.4	0.1	0.5
Top 13	11/15/2005	12/1/2005	16	25.7	4.1	25.5	0.7	1.0	6.6
Top 14	12/1/2005	12/16/2005	15	40.3	5.8	27.7	0.9	2.4	11.2
Top 15	12/16/2005	1/1/2006	16	107.0	5.2	22.6	0.8	5.5	24.2
Top 17	1/8/2006	1/16/2006	8	65.7	1.0	46.5*	1.6	6.3	30.5
Bot 1	2/8/2005	2/15/2005	7	397.7	6.5	44.7	1.2	25.6	177.8
Bot 2	2/15/2005	2/25/2005	10	466.9	5.7	46.6*	1.1	26.4	217.6
Bot 4	2/28/2005	3/15/2005	15	569.7	3.7	50.9*	0.7	20.8	290.2
Bot 7	4/15/2005	4/30/2005	15	550.9	5.4	39.4	1.0	29.9	217.1
Bot 9	5/31/2005	6/15/2005	15	32.8	13.5	9.2	2.2	4.4	3.0
Bot 10	6/15/2005	9/30/2005	107	216.7	3.0	17.6	0.5	6.6	38.1
Bot 12	11/1/2005	11/15/2005	14	230.2	1.3	27.0	0.2	3.0	62.2
Bot 14	12/1/2005	12/16/2005	15	83.1	1.6	26.4	0.3	1.3	21.9
Bot 15	12/16/2005	1/1/2006	16	233.5	1.9	28.5	0.3	4.4	66.5
Bot 16	1/1/2006	1/8/2006	7	372.9	3.0	43.0	0.5	11.2	160.2
Bot 17	1/8/2006	1/16/2006	8	712.5	5.0	39.7	0.8	35.6	282.5

Organic carbon concentrations ranged from 4.0% to 25.2% in the top trap and from 4.2% to 12.1% in the bottom trap (Table 3). Biogenic silica contents ranged from 0.7% to 34.5% in the top trap and from 14.9% to 35.6% in the bottom trap. The C/N molar ratio annual mean was about the same in both traps (7.5 – 7.6) and the SiO<sub>2</sub>/OC molar ratio mean increased from 0.4 at the surface to 0.9 at the bottom. Bio-silica fluxes reached their maximum value on March at both levels, organic carbon fluxes instead showed higher values during April at the top trap and during March at the bottom trap (Table 3).

**Table 3:** temporal series of mass, organic carbon and bio silica fluxes and of bio silica, organic carbon and nitrogen content related to mooring A 2008

Sample	Start	Stop	Days	Total flux (mg/(m <sup>2</sup> d))	%C org	%SiO <sub>2</sub> biogenic	%N	C flux (mg/(m <sup>2</sup> d))	Si flux (mg/(m <sup>2</sup> d))
Top 1	2/1/2008	2/15/2008	15	27.4	10.0	21.5	1.3	2.8	5.9
Top 2	2/15/2008	3/1/2008	14	14.5	25.2	9.3	4.5	3.4	1.3
Top 3	3/1/2008	3/31/2008	30	409.6	6.2	34.5	1.0	25.4	141.2
Top 4	3/31/2008	4/31/2008	31	346.8	9.3	31.0	1.5	33.4	107.4
Top 5	4/31/2008	5/31/2008	31	131.4	11.9	26.8	2.5	15.6	35.2
Top 6	5/31/2008	9/30/2008	122	135.1	6.3	10.6	0.8	8.5	14.3
Top 7	9/30/2008	11/1/2008	32	60.2	10.8	0.7	3.1	6.7	0.4
Top 8	11/1/2008	11/15/2008	14	11.8	19.4	10.0	4.4	2.3	1.2

Top 9	11/15/2008	12/1/2008	16	42.7	10.6	23.4	1.9	4.5	10.0
Top 10	12/1/2008	12/16/2008	15	27.7	4.0	25.1	0.7	1.1	7.0
Top 11	12/16/2008	1/1/2009	16	11.7	18.3	30.2	3.1	2.1	3.5
Top 12	1/1/2009	1/16/2009	15	9.6	13.9	20.4	2.3	1.3	2.0
Top 13	1/16/2009	2/1/2009	16	5.0	15.0	11.1	2.1	0.8	0.6
Bot 1	2/1/2008	2/15/2008	15	6.8	12.1	14.9	1.9	0.8	1.0
Bot 2	2/15/2008	3/1/2008	14	28.6	10.4	24.9	1.6	2.8	7.1
Bot 3	3/1/2008	3/31/2008	30	226.1	8.4	35.6	1.5	19.0	80.4
Bot 4	3/31/2008	4/31/2008	31	138.3	8.5	27.0	1.9	12.2	37.4
Bot 5	4/31/2008	5/31/2008	31	121.3	12.8	17.7	2.5	15.6	21.5
Bot 6	5/31/2008	9/31/2008	122	139.3	4.2	21.2	0.5	5.9	29.5
Bot 7	9/31/2008	11/1/2008	32	23.8	4.3	32.1	0.8	1.1	7.6
Bot 8	11/1/2008	11/15/2008	14	29.3	4.8	26.6	0.8	1.4	7.8
Bot 9	11/15/2008	12/1/2008	16	46.3	4.2	30.5	0.8	2.0	14.2
Bot 10	12/1/2008	12/16/2008	15	36.6	5.5	30.9	1.0	2.0	11.3
Bot 11	12/16/2008	1/1/2009	16	27.3	11.0	25.8	1.9	3.0	7.1
Bot 12	1/1/2009	1/16/2009	15	13.9	9.3	26.8	1.5	1.3	3.7
Bot 13	1/16/2009	2/1/2009	16	43.3	11.7	32.8	1.8	5.1	14.2

The amount of organic carbon and biogenic silica in the samples during each year reached about 50% of the vertical fluxes during the austral summer. In 2005 we can observe a predominance of lithogenic matter at both levels with higher values of about 70% from September to January and without significant differences in the sample composition at both levels (Fig. 3).



**Figure 3:** Sample composition at the two levels of mooring A during 2005 and 2008

During 2008 the top trap samples composition showed a high seasonal variability. In the first part of the year samples were mainly composed by lithogenic matter which represents about a half of the samples. From May 31 to November 15 samples were prevalently composed by  $\text{CaCO}_3$ , with concentrations ranging from 70% to 90%. From December 16 to February 1 the sample composition was more equally divided between all the constituents. In the bottom trap the pattern was more regular, with bio-silica percentage fairly constant. Compared to 2005 the percentage of  $\text{CaCO}_3$  during this year was much higher.

### 5.5.2 Swimmers

In 2005, the surface trap of mooring A contained very few organisms entered alive. They were mainly crustaceans and polychaetes, found especially in the second half of March, period that corresponds to the maximum flux of bio-silica and mass. Abundant empty or broken shells of pteropods of the species *Limacina helicina* and fecal pellets of various shapes and sizes have been found in late summer and early autumn samples; mucilaginous clusters were abundant especially from February to mid-March. It is worth mentioning that about half of the samples were composed of only passive flux.

Also in bottom samples organisms were not abundant. Crustaceans and polychaetes were, as in the top trap, the most numerous although several exemplar of hydromeduse have been found in second half of April samples. Most of the organisms were distributed from mid-April to the end of September, while the remaining samples consist only of passive flux (9 out of 14 samples consist entirely of passive flux). From February to the end of September many empty and broken shells of *Limacina helicina* have been found and, in samples from mid-April to late September, also some specimens probably came alive into the trap (from 200 to 420 specimens). The period of maximum abundance of organisms does not coincide precisely with that of maximum fluxes, as at the top trap, and except for the second half of April sample, the others show mass and biogenic fluxes quite low. In the top trap of mooring A 2008 the organisms have been determined as number of organisms/ml samples. The period of maximum abundance of organisms is from March to April. In the same periods many specimens of *Limacina helicina* have been found with the maximum peaks in March (192/ml) and April (68/ml).

The dinoflagellates concentrations are the highest between March, 1 and April, 30 (36 dinoflagellates/ml in March to 48 in April). Except for few specimens, the dinoflagellates counted are heterotrophs, feeding on diatoms and organic material.

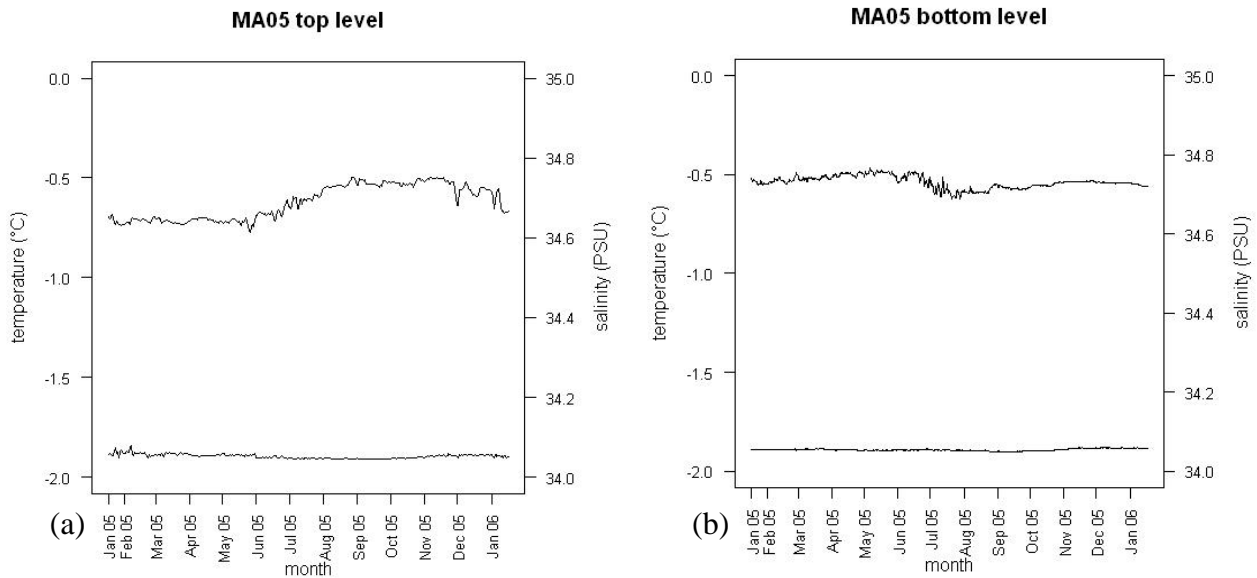
### 5.5.3 Physical parameters

MA 2005

At the top level (360 m), the temperature exhibited little excursions from January to June (mean -  $1.89^\circ\text{C}$ , max  $-1.84^\circ\text{C}$ , min  $-1.90^\circ\text{C}$ ). The salinity ranged from 34.61 to 34.7, with constant values of about 34.64 until June and an increasing to 34.74 values and more variability until January 2006 (Fig. 4a).



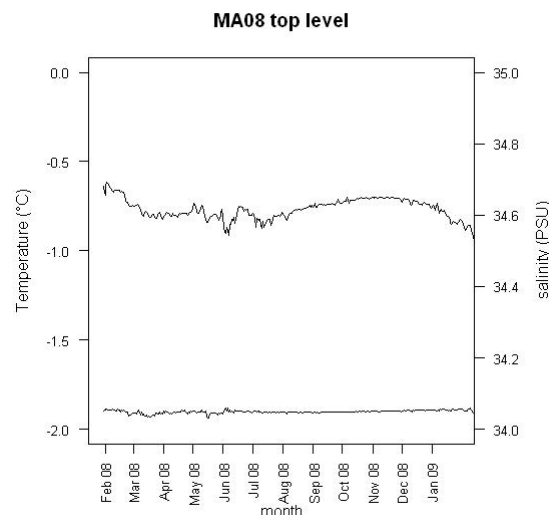
The temperatures recorded at the bottom level (770 m) showed quite constant values, slightly higher than  $-1.9^{\circ}\text{C}$  until November when the values have grown up until  $-1.88^{\circ}\text{C}$  for the rest of the year. Salinity values were quite variable from January 2005 to June around 34.74 then they began to decrease until August. From this time to the end of the year salinity values were constant with a mean value of 34.72 (Fig. 4b).



**Figure 4:** (a) temperature and salinity values recorded at the top level of instruments during 2005. (b) temperature and salinity values recorded at the bottom level of instruments during 2005.

## MA 2008

In the top level (370 m), the temperature values recorded oscillated around  $-1.9^{\circ}\text{C}$  (min  $-1.91^{\circ}\text{C}$ , max  $-1.89^{\circ}\text{C}$ ) with quite constant values during mid June through December 2008. From February to May 2008 the temperature records exhibited little excursions (mean  $-1.91^{\circ}\text{C}$ , max  $-1.88^{\circ}\text{C}$ , min  $-1.94^{\circ}\text{C}$ ).



**Figure 5:** temperature and salinity values recorded at the top level of instruments during 2008

On February we have registered the maximum value of salinity (34.69). This parameter decreased until March. Then, from March to June, it varied around 34.60. From June, it increased until November and then decreased again (Fig. 5).

#### 5.5.4 Sea ice

During 1994 the MA area has never been completely ice free. The sea ice concentration decreased from values of about 75-85% in November 1993 to around 7% at the end of December. It increased during January to 43% and then it decreased to a minimum value of about 4% at the end of February. From the end of February, the concentrations started to increase until reaching values higher than 90% at the end of March. The increase of the ice cover was then quite fast and it took about one month.

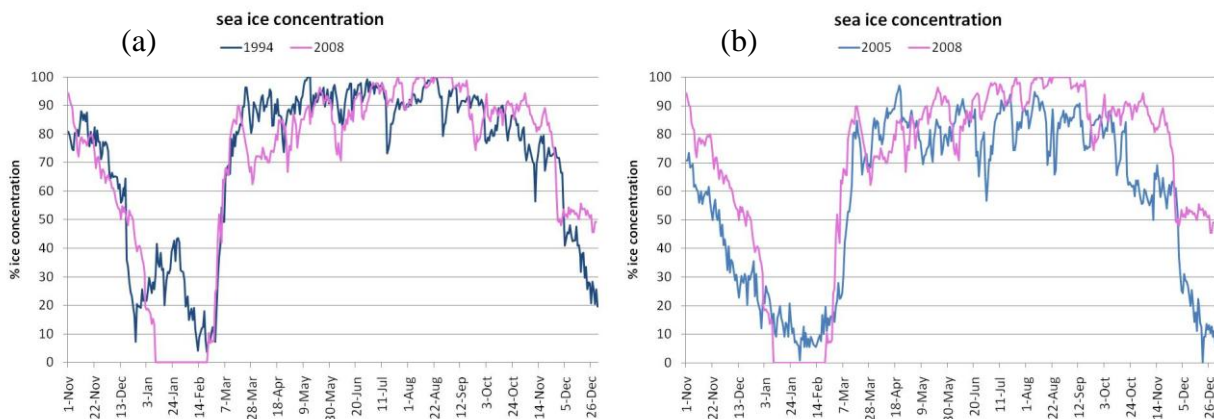
From April 1 to November 2 the values oscillated around an average of 90.5% with a maximum value of 100% and a minimum of 73.2%. During November the concentration values were around 70-75%, then they decreased to 20% at the end of December (Fig. 6a).

In 2005, the MA area has never been completely ice free probably due to the presence of the iceberg B-15. In 2000-2001 this iceberg of the size of 230x80 km<sup>2</sup> with an emerged part of 40 m and a draft of 300 m, broke off the Ross Ice Shelf, near the Ross Island, was transported by currents and remained between the Ross Island and the Beaufort Island for a period of five years (Arrigo et al., 2004).

The sea ice concentrations decreased from values of about 70-60% in November 2004 to around 10% between January and February, with a minimum of 0.8% on January 31. From the end of February, the concentrations started to increase until reaching values higher than 80% at the end of March and of 90% on April 18.

From April 18 to October 20 the values oscillated around an average of 82.6% with a maximum value of 97.2% and a minimum of 56.8%. The oscillations were thus quite wide. From October 20 the concentrations fell permanently below 80% and they took values approximately around 60% until the end of November. Then, at the end of December they decreased to values around 10% (Fig. 6b).

In early November 2007, the concentrations of ice were around values of 80-90% then they decreased until open sea conditions on January 10. So the area has remained completely ice free just over a month. From February 21 the ice grew rapidly to reach a concentration of 90% on March 18. From this moment the ice remained around an average concentration of 87.9% until November 24, when it finally lowered to less than 80%. In this period, the maximum value of concentration was 100%, reached for several days especially from the end of August to the beginning of September, while the minimum value was of 62.4%. From November 24 until the end of December, the concentrations were maintained around 50% (Fig. 6).

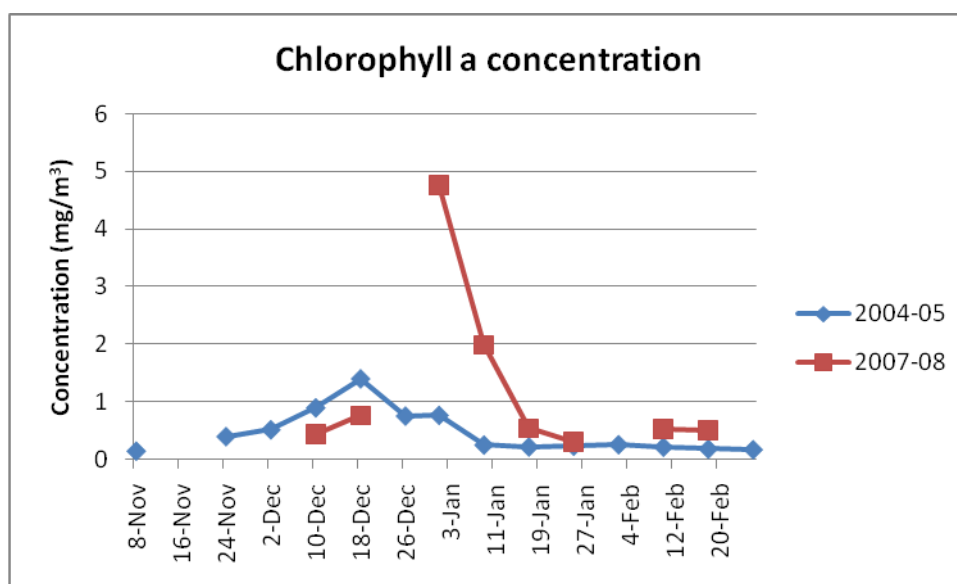


**Figure 6:** Sea ice concentrations during (a) 1994 and 2008 and (b) 2005 and 2008 over mooring A area

### 5.5.5 Chlorophyll a

We have examined chlorophyll a concentration data from November 8, 2004 to March 6, 2005 and from November 8, 2007 to March 6, 2008, periods of higher primary productivity. During 2004-2005 the concentrations increased gradually until the highest value reached from December 18, 2004 to December 25, 2004 ( $1.395 \text{ mg/m}^3$ ), then they decreased to a value around  $0.2 \text{ mg/m}^3$  from January to March (Fig. 9).

During 2007-2008 the data series is discontinuous with values higher then 2004-2005. The maximum value ( $4.767 \text{ mg/m}^3$ ) was reached in January 1, 2008 to January 8, 2008 (Fig. 7).



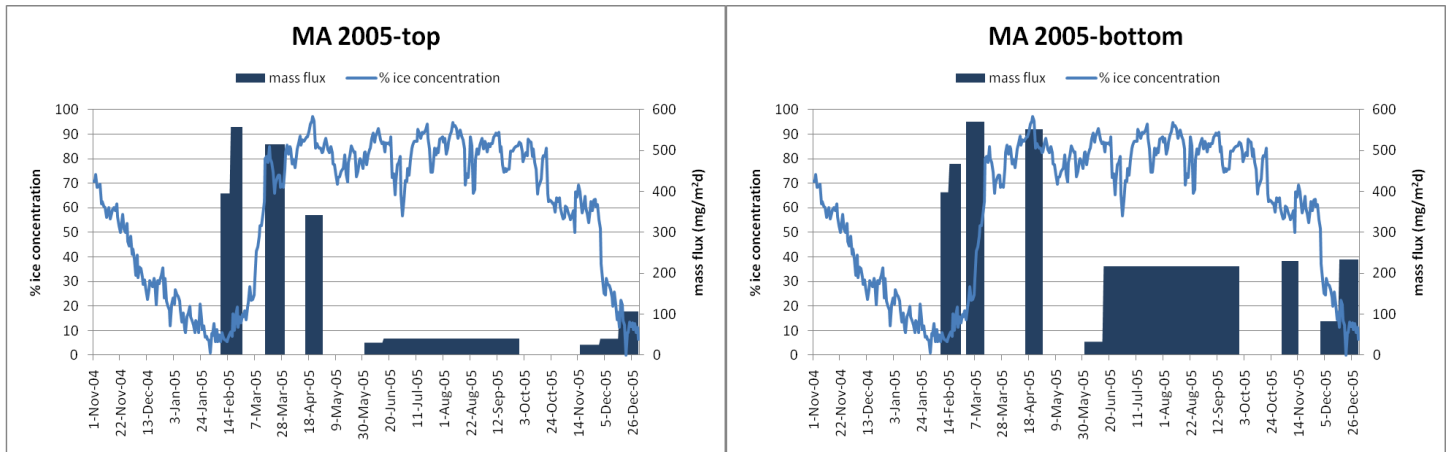
**Figure 7:** comparison between 2005 and 2008 chlorophyll a concentrations averaged on mooring A area

## 5.6 Discussion

### 5.6.1 Physical parameters and biological distribution

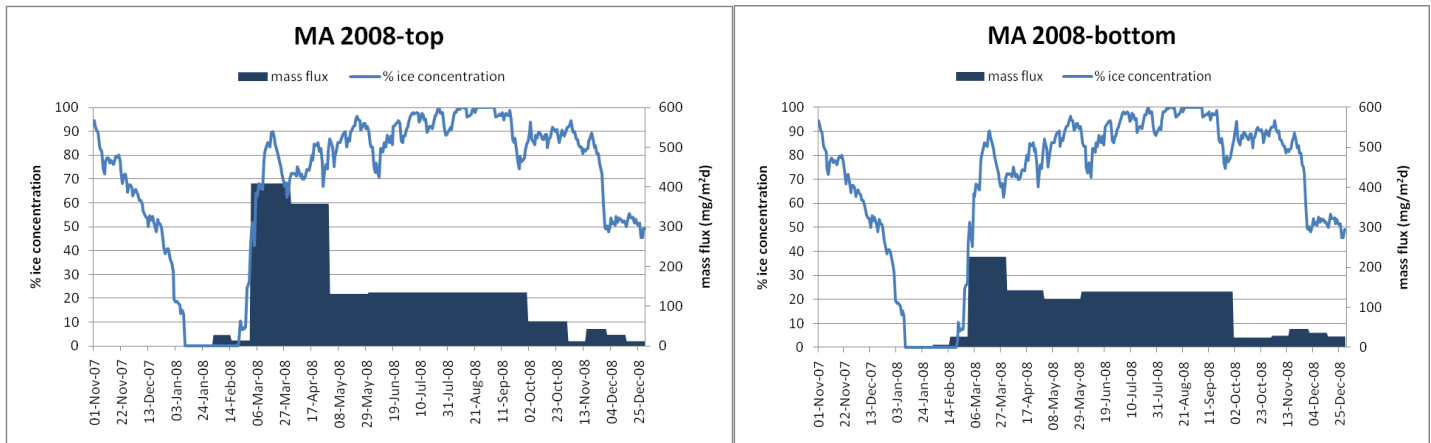
In figures 8 and 9 we show sediment fluxes and sea ice concentrations at both levels and during 2005 and 2008. In 2005, the maximum mass fluxes both at the top and at the bottom occurred before the period of maximum concentration of ice and during the days in which the ice was increasing. In the surface level, during the period of maximum stable concentration of sea ice, the trap has collected little material, with an average around 25 mg/(m<sup>2</sup>d) in the period from June to the end of November 2005. In December 2005, when the concentration of ice decreased, the material collected increased again and reached values of 107 mg/(m<sup>2</sup>d).

At the bottom, however, even in the period from June to December the trap has collected high amounts of material (141 mg/(m<sup>2</sup>d) on average), highlighting the presence of resuspension or lateral advection processes (Fig. 8).



**Figure 8:** Mass fluxes and sea ice concentration at the top and bottom levels during 2005

In 2008, the maximum mass flux peak, both at the top and bottom, coincided with the period of maximum ice concentration development. During winter the two traps have collected about the same amount of material (63 mg/(m<sup>2</sup>d) at the top and 60 mg/(m<sup>2</sup>d) at the bottom on average), this indicates that during this period the collection of material is mainly due to gravitational sinking along the water column (Fig. 9).



**Figure 9:** Mass fluxes and sea ice concentration at the top and bottom levels during 2008

In table 1 we show integrated data fluxes related to 2005 and 2008. We can note that in 2005 the fluxes were significantly higher in the bottom trap while in 2008 the fluxes were slightly higher at the surface level probably due to focusing and scouring processes respectively.

The only exception are the higher  $\text{CaCO}_3$  flux values at the top than at the bottom during 2005. This can be due to the greater amount of *Limacina helicina* empty shells found in the surface trap with respect to the bottom trap.

It should be noted, however, that while the 2008 data are complete, in the 2005 series there are different gaps in the two levels. If we compare the data integrated over 195 sampling days (Table 4), period in which samples are available for both levels (top and bottom), we can observe that a greater amount of material was collected into the bottom trap (a mass flux 2.43 times higher than the top if assessed globally and 2.39 times if evaluated on 195 days).

**Table 4:** Average particle fluxes during 2005 at Mooring A on 195 days.

Years	Level	Mass $\text{g}/(\text{m}^2\text{yr})$	Bio Si $\text{g}/(\text{m}^2\text{yr})$	OC $\text{g}/(\text{m}^2\text{yr})$	N tot $\text{g}/(\text{m}^2\text{yr})$	$\text{CaCO}_3$ $\text{g}/(\text{m}^2\text{yr})$	Lithogenics $\text{g}/(\text{m}^2\text{yr})$
2005	top	21.0	6.3	1.8	0.2	4.5	8.4
	bottom	50.1	14.4	2.0	0.4	3.3	28.2

In order to properly compare the annual integrated mass fluxes of 2005 with those of 2008 and 1994 (available in Langone et al., 2003) it is necessary to consider that the time series of 2005 samples is not complete and that, in particular, at the top trap we do not have the data of high flux periods (from February 25 to March 15 and from March 31 to April 15). Estimating around  $500 \text{ mg}/(\text{m}^2\text{d})$  the mass flux relative to the first 15 days of March and about  $350 \text{ mg}/(\text{m}^2\text{d})$  for the first 15 days of April we get an integrated mass flux on the year of  $54.9 \text{ g}/(\text{m}^2\text{yr})$ . These estimates were established taking into account the flux value of the periods immediately before and after and the typical mass flux related to these periods. The fluxes for the periods February 15 - February 25 and March 15 - March 31 were respectively  $557.30$  and  $514.16 \text{ g}/(\text{m}^2\text{d})$  and then we have considered an underestimation of  $500 \text{ g}/(\text{m}^2\text{d})$  for the in-between period. Similarly we have proceeded with the other time interval.

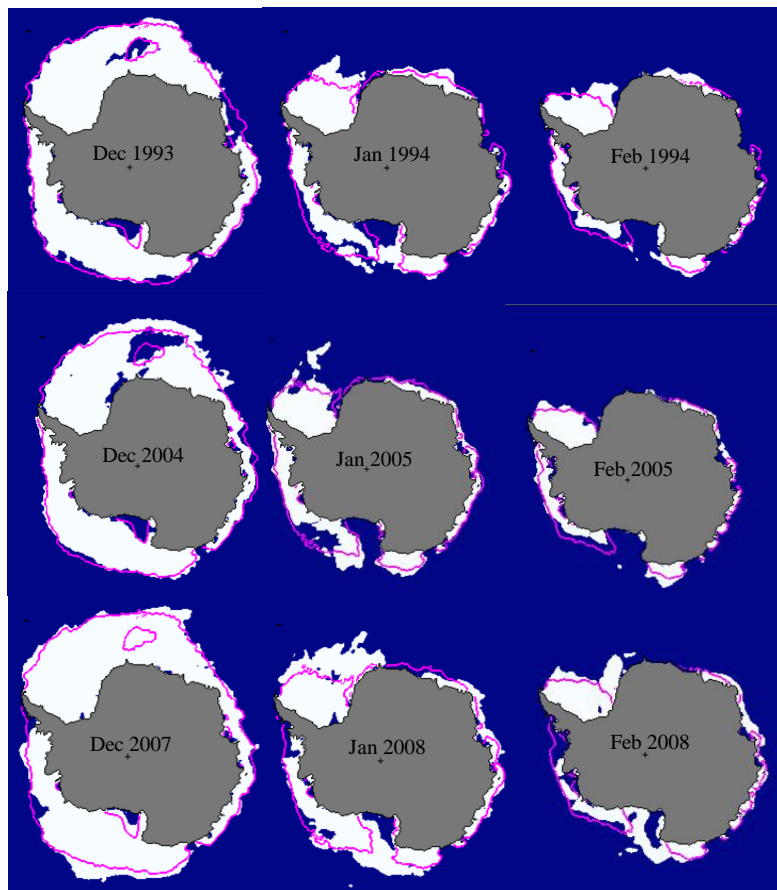
In 2005, the resulting flux is so comparable with the 1994 values and it is in agreement with the parameters of chlorophyll a concentrations, the sea ice extent and with the values obtained at the bottom that, with similar integration, achieve values of 113.2 g/(m<sup>2</sup>yr) (Table 5).

**Table 5:** Annual integrated mass and biogenic fluxes. 2005 fluxes are integrated over 257 days at the top and 229 days at the bottom.

Years	Level	Mass g/(m <sup>2</sup> yr)	Bio Si g/(m <sup>2</sup> yr)	OC g/(m <sup>2</sup> yr)
1994	top	59.3	26.3	10.6
	bottom	86.9	52.4	4.1
2005	top	42.2	15.0	2.3
	bottom	102.7	33.1	3.9
2008	top	47.8	10.8	3.8
	bottom	36.1	9.1	2.5

In 1994 (Langone et al., 2003), the samples composition was for 73% of bio-silica and OC, our fluxes data related to 2005 and 2008 differ greatly. If the mass values of 2005 fluxes are quite similar, this does not happen for the percentage composition. We have that the organic carbon and bio-silica were less than 50% and there was instead a predominance of lithogenic matter (Fig. 3). Also in 2008, the same thing occurred with the addition that the OC fraction was on average higher than in the other years (Table 3). This could suggest a less predominance of diatoms and a possible major development of *Phaeocystis antarctica* that has found most suitable conditions due to the high concentration and extension of sea ice (water less stratified and lower levels of irradiation (Arrigo et al., 1999)).

Comparing the sea ice concentrations in the mooring A area (Fig. 6) and the fluxes values (Table 5) in 1994, 2005 and 2008, it can be noted that during 1994 both sea ice concentrations and fluxes were high. During 2005 ice concentrations were lower and mass and biogenic fluxes quite high, while during 2008 sea ice concentrations were higher and fluxes lower. The sea ice extent in the Ross Sea in 2008 was higher than in 2005 and 1994 (Fig. 10). The high mass and biogenic fluxes recorded during 1994 may be due to higher productivity in the mooring A adjacent areas.



**Figure 10:** sea ice extension during summer in 1994, 2005 and 2008 (data were provided by the EOS Distributed Active Archive Center (DAAC) at the National Snow and Ice Data Center, University of Colorado, Boulder)

The peak of productivity in the Ross Sea usually is achieved in December or early January (Nelson et al., 1996; Smith et al., 2000; Arrigo and van Dijken, 2004). In 2005 the chlorophyll a maximum was in mid-December (Fig. 11) while in 2008 it was at the beginning of January (Fig. 12). In 2005, the mass flux peak occurred in February-March and in 2008 in March-April. A lag of two months between productivity and higher mass fluxes has already been highlighted (Dunbar et al., 1998; Collier et al., 2000) along with the possible causes such as a difference between the growth of phytoplankton and zooplankton community development (Dunbar et al., 1998; Smith and Dunbar, 1998; Boyd and Newton, 1999), a late bloom of diatoms associated to winds or pulse of iron (Collier et al., 2000; Peloquin and Smith, 2007), light aggregates of particles or a slower rate of sinking in the water column (Smith and Dunbar, 1998; Becquevort and Smith, 2001).

In 2005, we can assume that the delay in the mass flux was mainly related to zooplankton grazing because this is an area dominated by diatoms that are usually part of the food web unlike the *Phaeocystis antarctica* that is less grazed by zooplankton (Smith et al., 2003). In fact there were found abundant fecal pellets just in correspondence of the high flux of particulate material. In 2008, the further shift forward of about a month of the mass flux peak can be justified by a late opening of the sea ice in November and then a delayed algal bloom.

Comparing the values of chlorophyll a concentration in the two years considered, it can be seen that the highest concentrations around the mooring have occurred from December 26, 2004 to January 1,

2005 while in 2007-2008, after a first impulse with lower concentration from December 11 to December 19, 2007, the area was covered by the phytoplankton bloom from January 9 to January 16, 2008 (Figs. 11, 12).

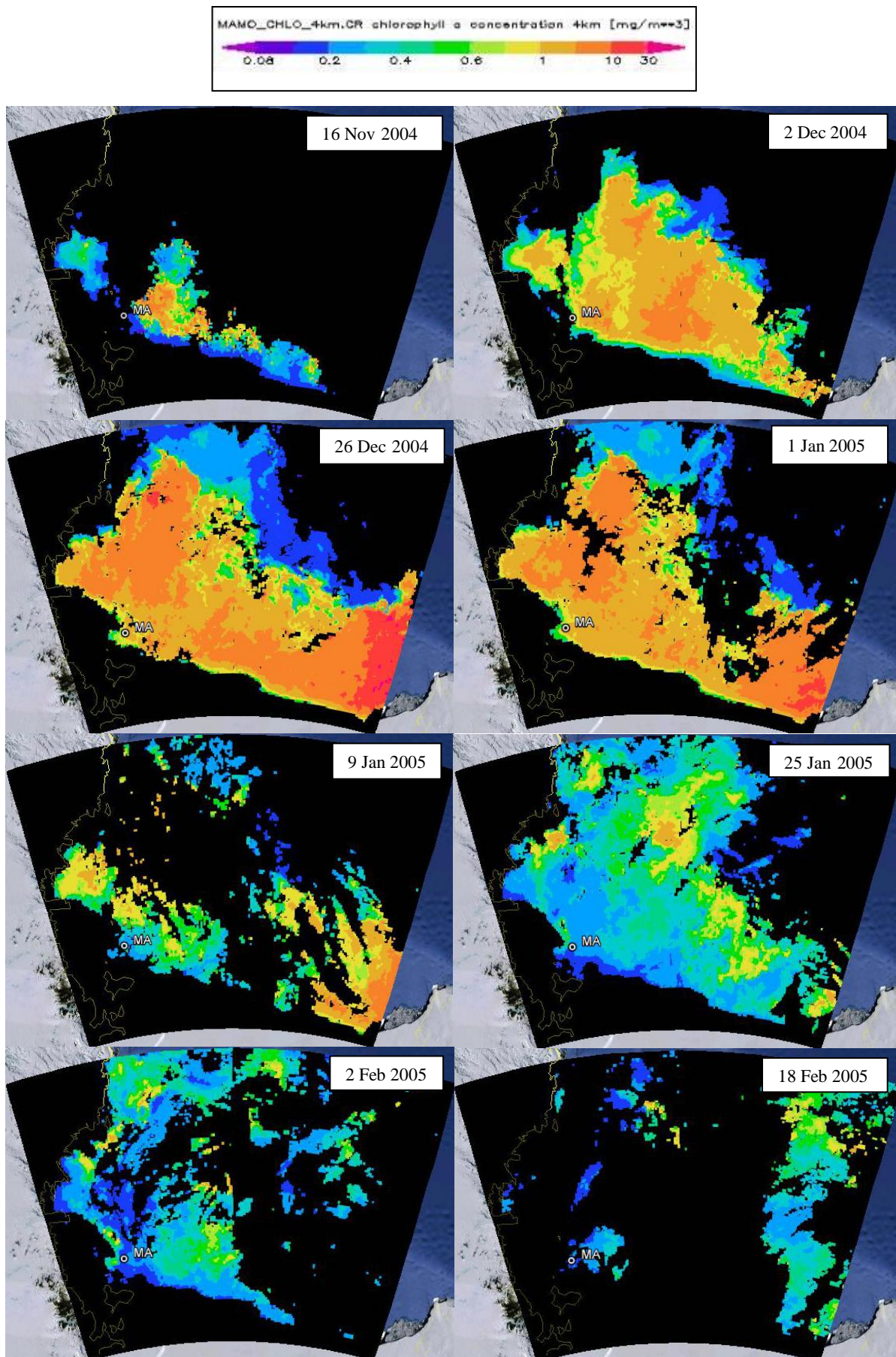
In 2008 the extent of the area with high chlorophyll a concentration (Fig. 12) has been very limited, probably due to the presence of sea ice. The mooring A area was affected by the presence of chlorophyll a only for 20 days in January and, also in the neighboring areas, the algal bloom has not had a wide extension. If we compare it with the extension and the concentration of chlorophyll a during 2005 (Fig. 11) the difference is evident: in 2005, the extension and concentration of chlorophyll a were significant by the end of November until the first week of January when the extension remained the same even if the concentration turned out to be much lower.

It can therefore be inferred that the phytoplankton bloom in 2005 had started at the end of November and that it lasted more than a month while in 2008, although the time length of the bloom was about the same considering the whole area, its extension was greatly reduced.

Comparing the chlorophyll a concentrations during the same days in 2005 and 2008 we can see some important differences: in the beginning of December 2005, the chlorophyll a has expanded to a great part of the western area and has had a concentrations above  $1 \text{ mg/m}^3$ . In 2008, however, around the Mooring A, concentrations were about the same but the chlorophyll a was spatially much more limited. In 2005, the chlorophyll a increased both in concentration and in extension until the end of December, little reducing in January. In 2008, the trend was about the same but with a restricted area reached by the chlorophyll a.

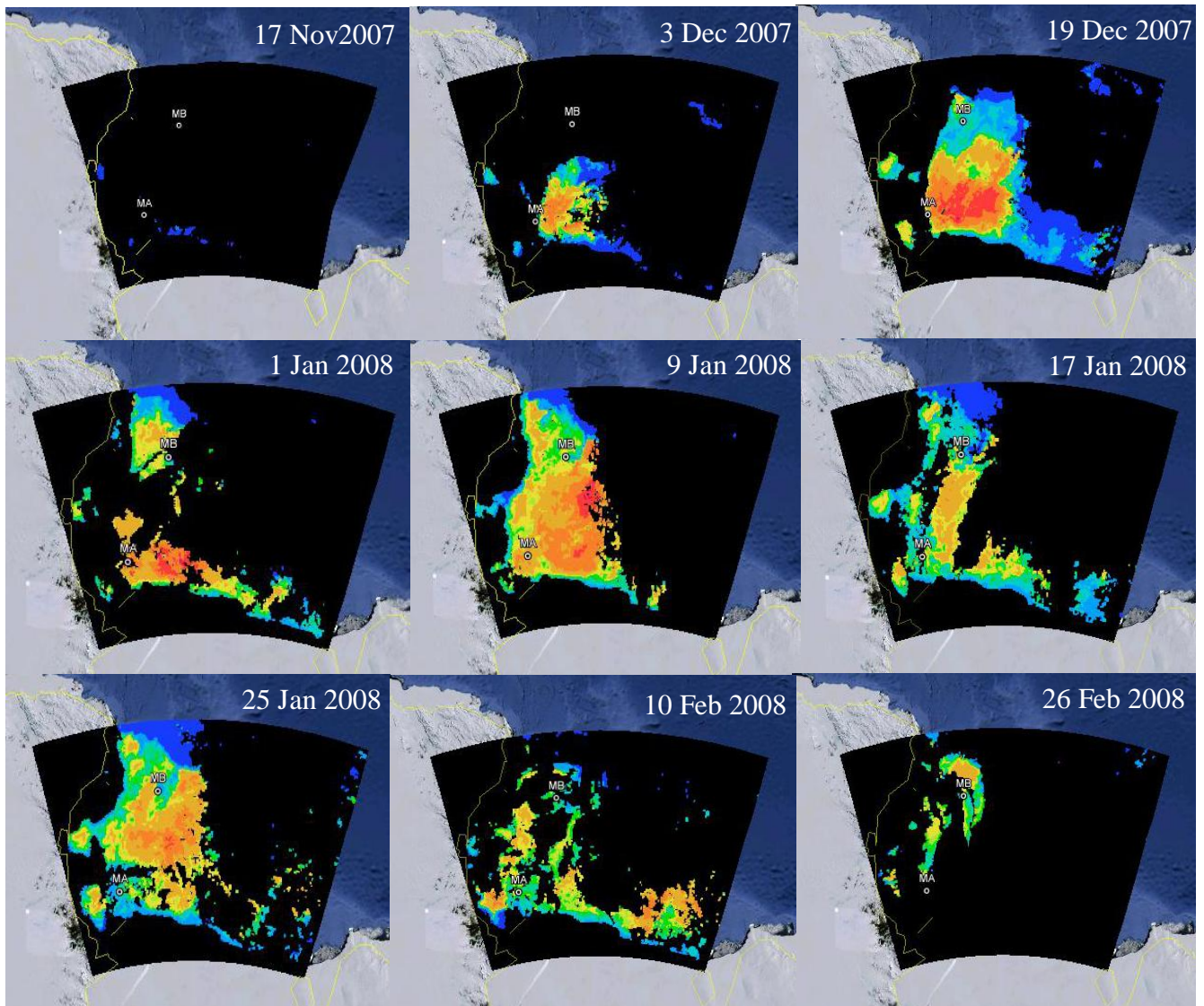
Looking at the satellite images of January 9, 17 and 25, 2008 (Fig. 12) it is evident the sharp margin that separates the area affected by chlorophyll a and the other one. The margin of chlorophyll a in fact coincided with the sea ice edge.





**Figure 11:** Chlorophyll a concentrations during 2004-2005





**Figure 12:** Chlorophyll a concentrations during 2007-2008

If we compare the concentrations of chlorophyll a in the area of mooring A during 2005 and 2008 we can see that the concentration values are higher in 2008, but shorter than in 2005 (Fig. 7).

In fact during 2008 the peak was at the beginning of January with a value of  $4.7 \text{ mg/m}^3$  while in 2005 the peak reached a value of only  $1.4 \text{ mg/m}^3$  (Fig. 7). But we have to underline that if in 2005 the presence of chlorophyll a in the area was constant from November to January it was not the same in 2008. The measurements by satellite did not record the presence of chlorophyll a from December 18 until January 3. This discontinuity is probably due to a shorter period in which the area was ice free and so the phytoplankton did not have a chance to develop itself.

Usually in the Ross Sea mass fluxes present two high peaks: the first due to the productivity that occurs when the ice melts and the second immediately after the ice formation due to the erosion of the pycnocline.

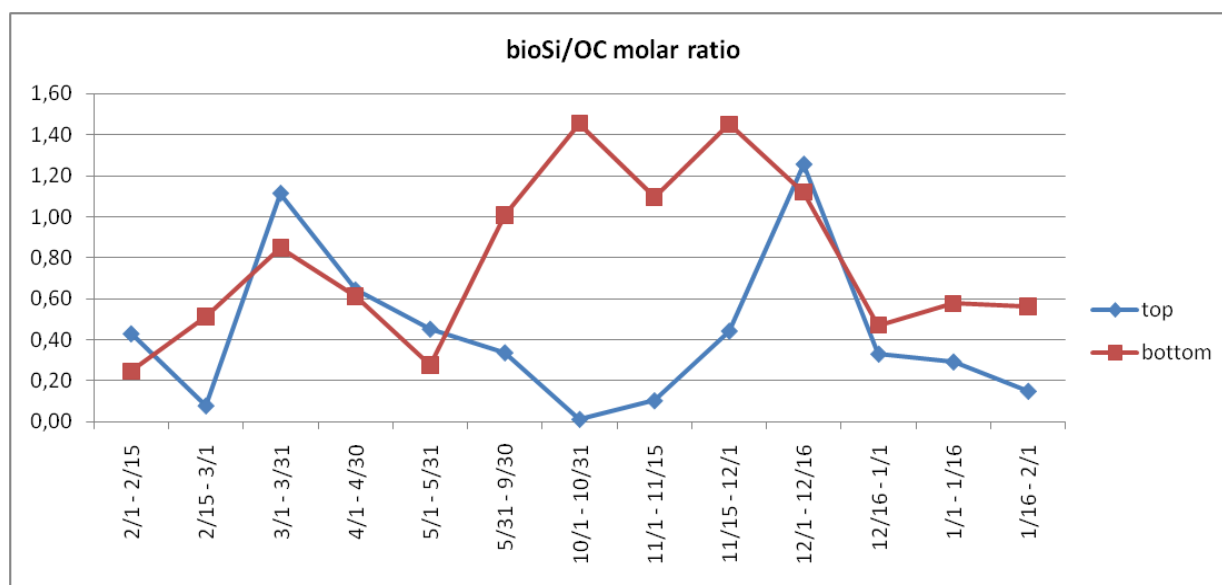
Looking at the mass peaks in 2005 we observe the first peak in mid-February and the second one in mid-March. In 2008 these two peaks are not distinguishable. The sea has been ice free later than usual and so the open sea period lasted less. For this reason the particle sinking has taken place all at once. Comparing the top and bottom flux values we observe that they can be considered equal

taking into account the measure error. This is due to the quick sank of the material that stayed in the upper water column for a shorter time and it has not have time to degrade.

If we compare the  $\text{SiO}_2/\text{OC}$  molar ratio data we note that in both years the values have highest average at the bottom than at the top (Table 1). In 2005, the average of this ratio was 1.0 at the top and 1.8 at the bottom and in 2008 it was 0.4 at the top and 0.9 at the bottom. Even comparing the entire time series of  $\text{SiO}_2/\text{OC}$  ratio the values observed are higher at the bottom than at the top, except for some cases (Fig. 13).

This confirms the decoupling of Si and C cycles (DeMaster et al., 1992), due to a greater degree of preservation of bio-silica compared to organic carbon along the water column.

This area of the Ross Sea has a substantial component of diatoms and Nelson et al. (1996) have obtained  $\text{SiO}_2/\text{OC}$  production ratio of about 0.60-0.65 on average in the ice edge diatoms bloom. The 2005  $\text{SiO}_2/\text{OC}$  values measured at 360 m were about twice this production ratio, while in 2008 the average ratio was only 0.4. This can be due, in addition to low productivity, to a very limited diatoms bloom and to the predominance of non siliceous algae.



**Figure 13:** Comparison between top and bottom  $\text{SiO}_{2(\text{bio})}/\text{C}_{\text{org}}$  molar ratios during 2008

During 2008 the peak of dinoflagellates concentration can be related to the peak of  $\text{SiO}_2/\text{OC}$  molar ratio. Probably the increase in dinoflagellates is related to a bloom in diatoms on which they feed or decaying organic material after a diatom bloom. The peak in dinoflagellates is synchronous to a peak in the cysts (resting stages) of the dinoflagellate *Polarella glacialis*, which lives in the Antarctic sea-ice (Montresor et al., 2003). Their highest occurrence (12 cysts/ml in April) matches with the period of maximum dinoflagellate occurrence and of partial decreasing in ice concentration after its fastest development during the month of March (Fig. 6).

The average of C/N molar ratio was about the same at both depths and in 2005 (with an average of 7.0 at the top and 7.2 at the bottom) and in 2008 (7.5 and 7.6 respectively at the top and bottom). This ratio is slightly lower than the Redfield ratio for Antarctic diatoms estimated about 8 (DeMaster et al., 1996). It is an indicator of resuspension processes (Collier et al., 2000); in fact nitrogen degrades more quickly than carbon and thus material resuspended from the bottom

presents higher values of this ratio. In our case, because the values remained constant in the two levels, it can be assumed that the resuspension processes were negligible. Furthermore because this values are slightly lower than the Redfield ratio estimated for diatoms it confirms the hypothesis of a rapid particle sinking and consequently low degradation.

The bottom waters in this area show the characteristics of High Salinity Shelf Water (HSSW) as regards temperatures but salinity values slightly lower. The HSSW originates in the polynia Terra Nova Bay and flows in the south-western part of the Ross Sea. It has a salinity of  $34.838 \pm 0.054$  and a temperature near the freezing point of  $-1.91 \pm 0.02^{\circ}\text{C}$  (Jacobs et al., 1985). Recent studies (Jacobs and Giulivi, 2010), however, have documented a freshening of the water masses in the Ross Sea and a decreasing of the salinity of the southwestern shelf of about 0.03 every ten years (Smith et al., 2012).

At the top, in both years, there were observed temperature values around  $-1.9^{\circ}\text{C}$  and salinity values from 34.60 to 34.74. Langone et al. (2003) found an important link between the fluxes of 1994 and physical changes occurred in the water column. These substantial changes in temperature and salinity were observed in surface waters. During 2005 and 2008 the top level was at a greater depth (350-360 m), so it is not possible to observe the same changes that occur in the first 200 m of the water column.

### 5.6.2 Mass balance

The availability of data of both level of sampling during 2005 and 2008 allows to carry out the mass balance in order to investigate the processes along the water column.

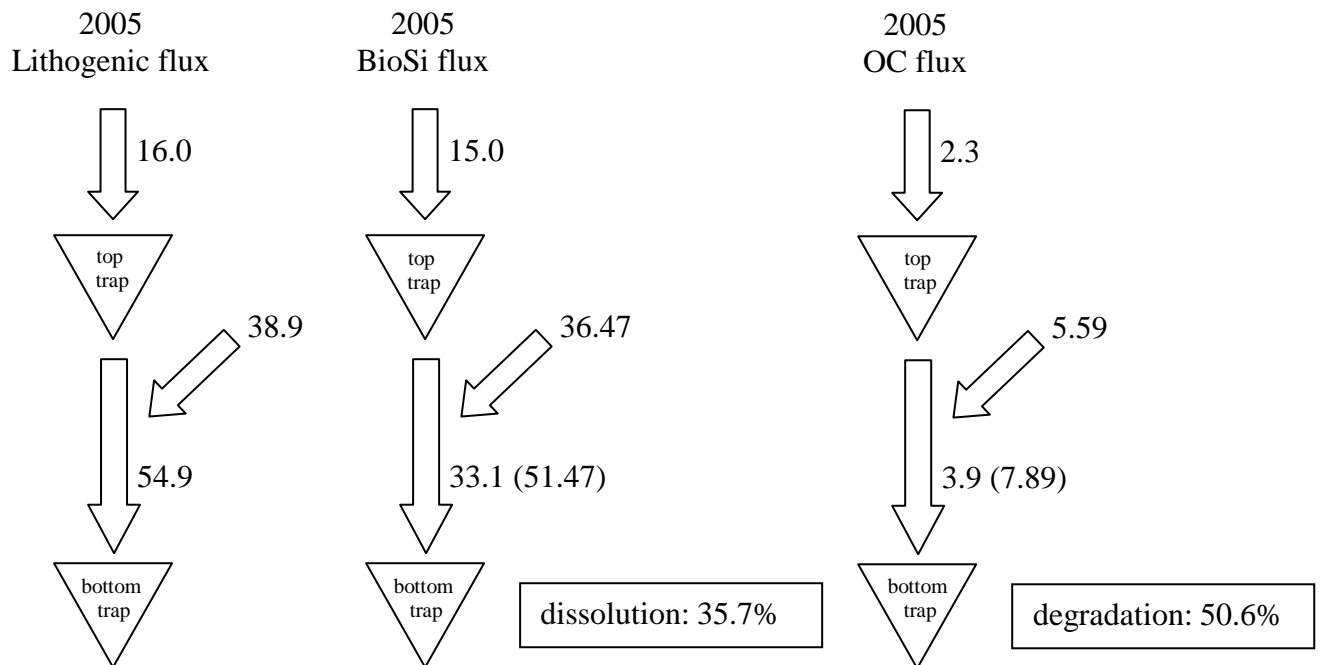
The mass balance is based on the assumptions that lithogenic fluxes are conservative and that the material laterally advected has the same composition of vertical flux. For this reason the values obtained have to be considered indicative.

Since the lithogenic material is the only one that does not undergo degradation during the sinking to the bottom it is used to determine the magnitude of lateral advection. It is considered as 100% the amount collected on the top, making the difference between the top and the bottom it is then determined the amount of material removed or focused. After this the fraction of material that not results from vertical sinking is determined.

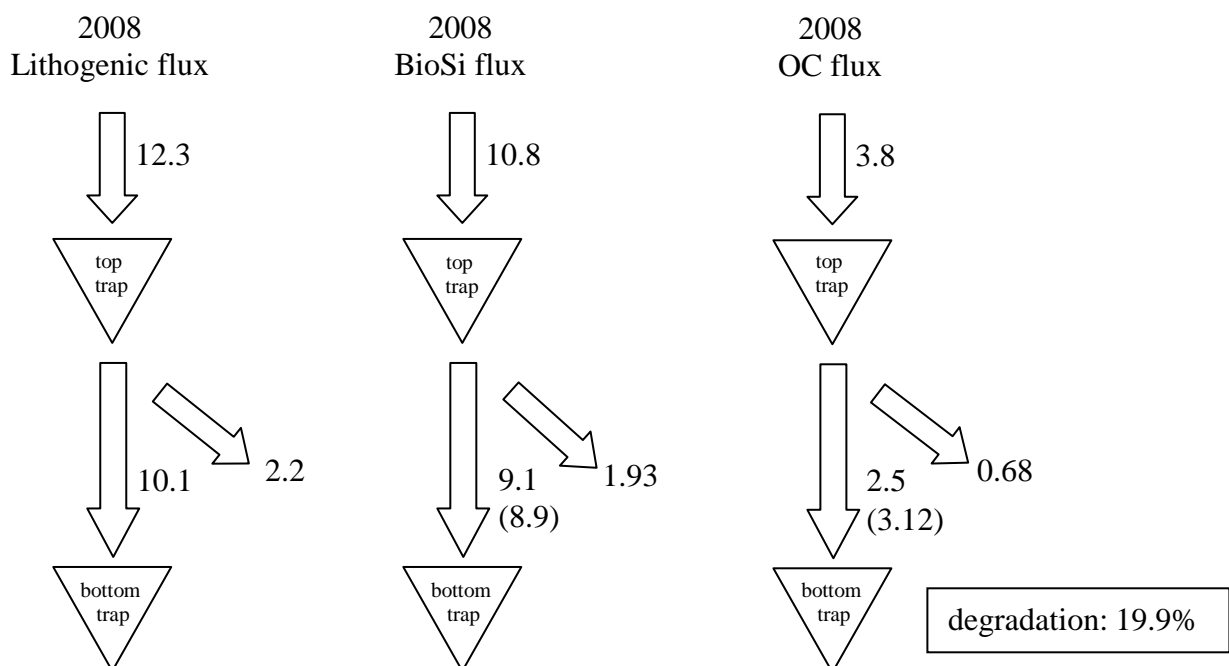
Assuming the material that arrives to the bottom trap has the same composition of the material due to the vertical flux, we may proceed to determine the amount of bio-silica and organic carbon focused or removed. To do this, we consider it removed or added with the same percentage of lithogenic with respect to the top level. The relationship between the Bio-Si and the OC amount collected in the bottom trap and the expected one (Figs. 14, 15) indicates the percentage of dissolution or degradation of the various elements along the water column.

The percentage of lithogenic material in 2005 did not show on average meaningful differences between the top and the bottom, ranging from 29.3% (with the exception of a value of 4.95% related to the first 15 days of June) to 70.29% at the top and from 21.71% to 71.83% at the bottom, so, despite the average annual lithogenic flux was much higher at the bottom, there was no difference between the percentage composition of the surface and deep samples.

If we compare the flux values at the top and bottom trap we can see that fluxes at the bottom are higher. This means that the material collected from the bottom trap is not the result only of vertical sinking along the water column but also of lateral advection processes.



**Figure 14:** Mass balance and processes of lateral advection. The numbers near the vertical arrows represent lithogenic, bio-silica and organic carbon annual integrated fluxes ( $\text{g}/(\text{m}^2\text{yr})$ ) at the top and bottom trap during 2005. The values near the sideways arrows represent lateral advection amount and numbers in brackets are the expected fluxes



**Figure 15:** Mass balance and processes of lateral advection. The numbers near the vertical arrows represent lithogenic, bio-silica and organic carbon annual integrated fluxes ( $\text{g}/(\text{m}^2\text{yr})$ ) at the top and bottom trap during 2008. The values near the sideways arrows represent the scoured amount and numbers in brackets are the expected fluxes

In 2005 there was an important lateral advection. In fact, the mass flux at the bottom level registered more than the double of the amount of material at the top. In 2008, the situation was the opposite: we find lower fluxes into the bottom trap.

In 2005, the contribution of lithogenic matter is equal to 2.43 times the vertical flux. Carrying out the balance of the bio-silica and the OC fluxes we get an expected value of silica of 51.47 g/(m<sup>2</sup>yr) against an actual value of 33.1 g/(m<sup>2</sup>yr) which would denote there was a dissolution of 35.7%. About organic carbon, the expected value is 7.89 g/(m<sup>2</sup>yr) against an actual value of 3.9 g/(m<sup>2</sup>yr) and then a degradation of 50.6% (Fig. 14). This underlines a well known phenomenon in these areas: the decoupling of carbon and silica cycles with a higher carbon degradation compared to silica dissolution (Nelson et al., 1996; Dunbar et al., 1998).

Since in 2005 the time series of samples was not complete, it has been remade the balance taking into account only the periods in which samples were both available, at the top and at the bottom level. The results show a dissolution of bio-silica of 31.9% and a degradation of organic carbon of 66.9%, thus confirming also in this case the decoupling between the two cycles.

In 2008, as already said, fluxes into the bottom trap were lower than those at the surface, even if the difference is rather low since 2008 was a year characterized by low fluxes of particles in general.

The balance in this case leads to no dissolution for the silica, in fact, the expected value is 0.2 g/(m<sup>2</sup>yr) less than the actual value, taking into account the errors of measurement, these two values can be considered equals. Organic carbon has an expected value of 3.12 g/(m<sup>2</sup>yr) with an actual value of 2.5 g/(m<sup>2</sup>yr). The organic carbon degradation is in this case of 19.9% (Fig. 15). This value is much lower than the one of 2005.

At the top level particle fluxes during 2005 and 2008 do not differ a lot. In 2005 they were slightly higher. This difference is due to a higher primary productivity deducible from the chlorophyll a values (Figs. 11, 12). Comparing the bottom levels, on the contrary, it can be observed that the particle fluxes values in 2005 were significantly higher than in 2008.

As a result of the bio-silica and organic carbon fluxes balance, lateral advection in 2008 was probably negligible. This may be due to the low primary productivity that has characterized the entire area of the Ross Sea and to a lower hydrodynamics during this year.

During 2008, the ice concentration was greater than in 2005 and the Ross Sea was never completely ice free (Fig. 10). The greater amount of sea-ice that have surrounded the Ross Sea during summer has certainly influenced surface and bottom waters causing a reduced hydrodynamics.

It is worth mentioning that in 2005 the iceberg B-15 was positioned near the mooring A area. This iceberg has changed the hydrodynamics of the area (Van Woert et al., 2003) and may have caused a greater supply of lithogenic material.

## 5.7 Conclusions

The analysis of particle fluxes, of sea ice and chlorophyll a concentrations carried out on two years (2005 and 2008) of samples from the mooring A located in the Ross Sea and the comparing of these with the results on the 1994 samples reported in literature document the seasonal and inter-annual variability in these regions.

The mass and biogenic fluxes were highest in February and March, a couple of months later the algal blooms that usually occur on December - January as evidenced by the maximum value of chlorophyll a concentrations related with the processes of ice formation and melting.

During the 2005 year two high peaks of the mass fluxes (February and March) occur in the Ross Sea, whereas in 2008 we observed only one peak (March) due to the shorter period in which the sea was free of ice.

From February to April, at the top level and in both years, the trap collected about 50% of the annual mass flux. In the same period we find the highest silica percentages. Biogenic fluxes followed the trend of mass fluxes at both levels.

The inter-annual variability is particularly highlighted by the different fluxes magnitude and percentage composition of the material collected in the traps. Large differences were found at the bottom level with annual average values of mass flux equal to 86.9 g/(m<sup>2</sup>yr) in 1994, 102.7 g/(m<sup>2</sup>yr) in 2005 and 36.1 g/(m<sup>2</sup>yr) in 2008 despite differences at the top level below 17 g/(m<sup>2</sup>yr).

The mass balance between top and bottom traps underlines the absence of lateral advection processes during the 2008. On the contrary these processes are documented during the 2005.

The most probable cause is related to differences in the extent and concentration of ice. If the period in which the sea is ice free is too short, bloom of phytoplankton does not have enough time to develop, and this affects the development of zooplankton and the whole food web. The values of chlorophyll a concentrations confirm this hypothesis, in fact, in 2008 the maximum value was much higher than the 2005 one, but it lasted less than half, so even if there has been a high development of phytoplankton this not had the opportunity to grow and expand as it did in 2005. Furthermore the presence of greater extension of ice surrounding the Ross Sea has inhibited the hydrodynamics. This has consequently reduced the lateral advection processes.

Despite the same ice concentration in the mooring A area during 1994 and 2008, mass fluxes were more than twice at the bottom trap in 1994. This can be due to the greater extension of the polynia during 1994 that may imply the presence of a greater algal bloom extension near the mooring A area.

Even if the temporal range from 1994 and 2008 is quite long the comparison only between three years (1994, 2005 and 2008) is not enough to identify a flux trend to explain the inter-annual variability.

Since it seems that the physical parameters related to the formation and melting of ice are strongly linked to the magnitude of the mass and biogenic fluxes, climate changes may strongly influence the biogeochemical cycles and then change the uptake of CO<sub>2</sub>. So particle fluxes analysis may be useful to monitor climate changes in Antarctica.

## Acknowledgments

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## General conclusions

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The analysis of Ross Sea sediment trap samples collected in two moorings, A and B, deployed respectively in the south-western polynia area and in the Joides Basin in the north-western of the Ross Sea (Antarctica) has been used to investigate biogeochemical cycles variability. The seasonal, inter-annual and regional variability that characterizes these areas have been then related to changes in the extension and concentration of ice and consequently to the extra Antarctic atmospheric circulation (ENSO).

For this purpose the Heussner method for the preparation of sediment trap samples in use at ISMAR-CNR Bologna has been modified to make it more efficient without reducing the precision. The method developed has been achieved by modifying some steps which derive from the procedures in use at Stanford University.

The parameters used to investigate the seasonal, inter-annual and regional variability are: the mass and biogenic fluxes, the composition of the trap samples, the cataloguing of the swimmers, the determination of the  $\text{SiO}_2/\text{OC}$  and C/N molar ratios and the fluxes mass balance. The results have been then compared with the physical and chemical characteristics of water and with satellite derived data (concentration and extent of sea ice, concentration of chlorophyll a, concentration of diatoms) in order to identify possible correlations between climatic factors and variability of biogeochemical cycles.

The analysis of all samples and in both areas has highlighted a high seasonal variability both in terms of the mass and biogenic fluxes and for the percentage composition of the samples. High fluxes were recorded in late summer and early autumn, about two months after the algal bloom, and very low fluxes were recorded when the sea ice cover was total. Bottom traps showed higher fluxes than the upper ones in periods of total ice cover, and this made it possible to detect the presence of lateral advection processes at both sites. Finally, the percentage composition of the samples shows significant changes during the year, particularly at the top level.

The inter-annual variability has been studied by comparing the data obtained from the particles collected at site B during 1996, 1998, 1999, 2005 and 2008 and at site A during 2005 and 2008. The values of fluxes and the samples composition confirm the high inter-annual variability of the biogeochemical cycles in the Ross Sea. The comparison of flux data with the satellite data concerning the sea ice concentration and extent and the chlorophyll a and diatoms concentration over such a long period allowed to identify a correlation between these parameters. In particular sea ice extension changes seemed to have a cyclicity on decadal scale, this has led to compare them with the climatic fluctuations related to ENSO.

It was thus identified a positive correlation to ENSO during 1996 and 1999 (years subjected to La Niña events) which show low sea ice concentrations and 1998 (year subjected to El Niño event) that shows a high extent of the sea ice. The next decade, instead, shows negative correlation with ENSO fluctuations. This is in agreement with previous studies in which, in the Marie Byrd Land, the atmospheric response to ENSO fluctuations shows a reversal about every 10 years.

The comparison between samples at site A and B in 2008 made it possible to identify the differences that characterize these two areas (regional variability): higher flux values in the polynia (MA) compared to the north west region of the Ross Sea (MB). There was no evidence, however, of some unique characteristics of Joides Basin where mooring B was deployed: lateral advection contribution of materials from the near bank at the bottom level and high rates of bio-silica accumulation. In 2008, the great sea ice coverage has led to low primary productivity and lower hydrodynamics resulting in inhibition of the processes of lateral advection and on average lower fluxes.

In addition, during 2008 the great sea ice concentration has inhibited primary productivity not only in the area of mooring A, but all over the southern sector of the Ross Sea. So it has not allowed the regular development of phytoplankton.

Usually in the Ross Sea the maximum particle sinking occurs in two subsequent steps: the first due to algal bloom that develops during the ice melting and the second due to the erosion of the pycnocline during the ice formation processes.

So while in 2005 the mass fluxes showed both peaks, in 2008 it is possible to identify only one. The short period during which the sea was ice free has not allowed the development of phytoplankton, so the particles have fallen all at once.

## Appendix

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### Analytical procedure for biogenic silica analysis

The method used to determine the biogenic silica percentage in sediment trap samples is the DeMaster modified method (1981). This method is based on the different behaviour in basic solution of the biogenic silica with respect to the mineral one, which have different dissolution rates.

Analytical procedure for the biogenic silica analysis:

- 1) weigh about 20 mg of each sample in tubes of Teflon. Along with each set of samples it is necessary to analyze a blank and a standard;
- 2) in each tube add 35 ml of 0.5 M NaOH and stir vigorously;
- 3) immerse the tubes in a water bath at 85°C while stirring the tubes at least every 20 minutes;
- 4) after one hour remove the tubes and centrifuge for 3 minutes at 2000 rpm;
- 5) prepare a first series of tubes containing water;
- 6) take from each tube 0.2 ml of supernatant and place them in the first series of tubes;
- 7) repeat the procedure from step 5 for 2 more times;
- 8) fill the first set of tubes with water until it reaches 5 ml;
- 9) prepare a second set of tubes containing 0.16 ml of 0.5 M NaOH and 1.84 ml of water;
- 10) take 1 ml from the first series and place it in the corresponding tube of the second series;
- 11) add 0.8 ml of ammonium para-molybdate in all the tubes of the second series, mix vigorously and wait 10 minutes;
- 12) prepare the reducing solution and add 1.2 ml of it in each tube of the second series;
- 13) mix immediately and wait 3 hours;
- 14) measure with the spectrophotometer the absorbance of the solutions (wavelength: 810 nm).

#### Standards

- 1) prepare 6 solutions with known concentrations of biogenic silica
- 2) prepare 7 tubes (1 white and 6 standards) containing: 2.8 ml of water and 0.2 ml of the solutions at known concentration; in the white put 0.2 ml of 0.5 M NaOH;
- 3) put 0.8 ml of ammonium paramolybdate in each tube and mix vigorously;
- 4) wait 10 minutes and add 1.2 ml of reducing solution;
- 5) shake vigorously and wait 3 hours for the measurement with the spectrophotometer (wavelength: 810 nm).

#### Reducing solutions

Mix together 100 ml of metol-sulfite and 60 ml of saturated solution of oxalic acid. Mix slowly adding 60 ml of sulfuric acid.

With methods of linear interpolation, using a software, it is obtained an absorbance-concentration function of the standards by which it is possible to obtain the silica concentration of the samples; from the release curve of the silica as a function of time one can extrapolate that of biogenic silica eliminating the contribution of the silica mineral.

## **Organic Carbon analysis**

For the analysis of organic carbon we use a gas chromatograph CHN Elemental Analyzer coupled to a mass spectrometer for isotopic ratios. The sample is pretreated with hydrochloric acid in order to eliminate the fraction of carbonates (calcite and aragonite). The mass spectrometer is used to determine the ratios of the carbon ( $\delta^{13}\text{C}$ ) and nitrogen ( $\delta^{15}\text{N}$ ) stable isotopes while the gas chromatograph returns the percent value of carbon and nitrogen.

## Sample composition

(AT = mooring A top trap, AB = mooring A bottom trap, BT = mooring B top trap, BB = mooring B bottom trap, Red values = anomalous values)

sample	Period	days	Mass (mg)	Silice (%)	OC (%)	N (%)	CaCO3 (%)	Lito (%)	mass flux (mg/(m <sup>2</sup> d))	Bio-silica flux (mg/(m <sup>2</sup> d))	OC flux (mg/(m <sup>2</sup> d))
AT05_01	08/02 - 15/02	7	1382.96	39.51	6.33	1.175	14.6	33.25	395.13	156.12	25.01
AT05_02	15/02 - 25/02	10	2786.48	44.78	6.44	1.150	13.1	29.25	557.30	249.57	35.87
AT05_05	15/03 - 31/03	16	4113.28	49.5	4.61	0.838	10.1	31.16	514.16	254.51	23.69
AT05_07	15/04 - 31/04	15	2571.12	22.47	2.33	0.898	42.7	30.12	342.82	77.03	19.37
AT05_09	31/05 - 15/06	15	226.13	0.33	4.72	0.754	85.3	4.95	30.15	0.10	1.42
AT05_10	15/06 - 31/09	107	2120.16	18.69	2.00	0.871	17.3	59.96	39.63	7.41	2.18
AT05_11	31/09 - 1/11	32	30.91	23.82	2.38	0.365	1.1	70.29	1.93	0.46	0.05
AT05_13	15/11 - 1/12	16	205.95	25.51	4.05	0.735	0.6	65.77	25.74	6.57	1.04
AT05_14	1/12 - 16/12	15	302.2	27.71	5.83	0.928	3.4	57.24	40.29	11.17	2.35
AT05_15	16/12 - 1/01	16	855.92	22.61	5.16	0.803	1.3	65.74	106.99	24.19	5.52
AT05_17	8/01 - 16/01	8	262.64	46.51	1.04	1.584	3.8	47.64	65.66	30.54	6.30
AB05_01	08/02 - 15/02	7	1391.84	44.7	6.45	1.149	4.2	38.25	397.67	177.76	25.64
AB05_02	15/02 - 25/02	10	2334.32	46.6	5.65	1.101	11.5	30.57	466.86	217.56	26.37
AB05_04	15/03 - 31/03	15	4272.48	50.94	3.65	0.714	10.6	31.12	569.66	290.19	20.79
AB05_07	15/04 - 31/04	15	4132.08	39.41	5.42	1.036	16.0	33.74	550.94	217.13	29.87
AB05_09	31/05 - 15/06	15	246.13	9.18	13.53	2.159	42.0	21.71	32.82	3.01	4.44
AB05_10	15/06 - 31/09	107	11593.84	17.56	3.03	0.491	4.5	71.83	216.71	38.05	6.57
AB05_12	31/09 - 1/11	14	1611.57	27.03	1.30	0.225	1.1	69.29	230.22	62.23	2.99
AB05_14	15/11 - 1/12	15	623.3	26.36	1.56	0.261	0.4	70.11	83.11	21.91	1.29
AB05_15	1/12 - 16/12	16	1867.76	28.49	1.89	0.310	0.6	67.14	233.47	66.52	4.41
AB05_16	16/12 - 1/01	7	1305.2	42.96	3.00	0.481	0.1	50.97	372.91	160.20	11.19
AB05_17	8/01 - 16/01	8	2850	39.65	4.99	0.753	0.8	49.54	712.50	282.51	35.56
AB05_18	16/01 - 24/01	8	0	35.66	11.63	1.565	3.9	37.13	0.00	0.00	0.00

sample	Period	days	Mass (mg)	Silice (%)	OC (%)	N (%)	CaCO3 (%)	Lito (%)	mass flux (mg/(m <sup>2</sup> d))	Bio-silica flux (mg/(m <sup>2</sup> d))	OC flux (mg/(m <sup>2</sup> d))
AT08_01	2/1-2/15	15	410.67	21.5	10.03	1.28	9.95	48.49	27.38	5.90	2.75
AT08_02	2/15-3/1	14	202.67	9.3	25.17	4.48	4.21	36.15	13.51	1.34	3.40
AT08_03	3/1-3/31	30	12288.00	34.5	6.19	1	4.17	48.95	409.60	141.17	25.37
AT08_04	4/1-4/30	31	10752.00	31	9.33	1.54	5.68	44.66	358.40	107.39	33.44
AT08_05	5/1-5/31	31	4072.00	26.8	11.85	2.46	34.55	14.95	131.35	35.17	15.57
AT08_06	5/31-9/30	122	16480.00	10.6	6.27	0.77	91.61	0.00	135.08	14.27	8.47
AT08_07	10/1-10/31	32	1925.33	0.7	10.80	3.08	95.43	0.00	62.11	0.42	6.71
AT08_08	11/1-11/15	14	165.33	10	19.36	4.37	49.47	1.81	11.81	1.18	2.29
AT08_09	11/15-12/1	16	682.67	23.4	10.59	1.9	29.78	25.64	42.67	9.99	4.52
AT08_10	12/1-12/16	15	416.00	25.1	4.01	0.7	36.48	30.40	27.73	6.96	1.11
AT08_11	12/16-1/1	16	186.67	30.2	18.30	3.14	16.41	16.79	11.67	3.52	2.13
AT08_12	1/1-1/16	15	144.00	20.4	13.91	2.29	15.71	36.07	9.60	1.96	1.34
AT08_13	1/16-2/1	16	80.00	11.1	14.99	2.1	28.83	30.09	5.00	0.56	0.75
AB08_01	2/1-2/15	15	101.33	14.9	12.08	1.89	45.85	15.09	6.76	1.01	0.82
AB08_02	2/15-3/1	14	400.00	24.9	10.41	1.57	31.03	23.25	26.67	7.11	2.77
AB08_03	3/1-3/31	30	6784.00	35.6	8.40	1.48	13.45	34.15	226.13	80.44	19.00
AB08_04	4/1-4/30	31	4288.00	27	8.54	1.89	34.04	21.88	142.93	37.39	12.20
AB08_05	5/1-5/31	31	3760.00	17.7	12.83	2.54	52.00	4.64	121.29	21.50	15.56
AB08_06	5/31-9/30	122	16992.00	21.2	4.21	0.51	41.43	28.95	139.28	29.54	5.86
AB08_07	10/1-10/31	32	762.67	32.1	4.25	0.77	5.51	53.89	24.60	7.64	1.05
AB08_08	11/1-11/15	14	410.67	26.6	4.83	0.81	10.45	53.29	29.33	7.79	1.42
AB08_09	11/15-12/1	16	741.33	30.5	4.21	0.76	14.79	46.29	46.33	14.15	1.95
AB08_10	12/1-12/16	15	549.33	30.9	5.51	1	20.04	38.04	36.62	11.31	2.02
AB08_11	12/16-1/1	16	437.33	25.8	10.97	1.88	20.98	31.28	27.33	7.06	3.00
AB08_12	1/1-1/16	15	208.00	26.8	9.31	1.53	13.76	40.82	13.87	3.72	1.29
AB08_13	1/16-2/1	16	693.33	32.8	11.66	1.76	12.63	31.25	43.33	14.20	5.05



sample	Period	days	Mass (mg)	bio-Silica (%)	OC (%)	N (%)	CaCO3 (%)	Lito (%)	mass flux (mg/(m <sup>2</sup> d))	Bio-silica flux (mg/(m <sup>2</sup> d))	OC flux (mg/(m <sup>2</sup> d))
BT96_01	26/01-16/03	50	4068.50	54.0	8.6	1.4	12.4	16.3	162.74	87.88	14.07
BT96_02	16/03-01/05	46	62.10	27.5	10.2	2.0	4.0	48.1	2.70	0.74	0.27
BT96_03	01/05-01/06	31	65.41	4.3	13.6	3.2	39.9	28.7	4.22	0.18	0.57
BT96_04_05	01/06-01/10	122	48.19	3.5	10.0	2.0	45.6	30.9	0.79	0.03	0.08
BT96_06	01/10-7/11	37	37.93	12.2	6.2	1.2	40.6	34.9	2.05	0.25	0.13
BT96_07	07/11-01/12	24	103.68	39.5	6.8	1.2	31.0	15.9	8.64	3.41	0.58
BT96_08-10	01/12-16/01	46	60.26	26.7	10.9	1.8	20.9	30.6	2.62	0.70	0.29
BT96_11	16/01-20/12	338	91.26	6.3	10.1	1.6	72.1	1.4	0.54	0.03	0.05
BB96_01	26/01-5/02	10	684.55	52.0	7.4	1.1	5.5	27.7	136.91	71.19	10.18
BB96_02	5/02-15/02	10	64.80	40.1	9.8	1.4	2.9	37.3	12.96	5.20	1.27
BB96_03	15/02-1/03	15	913.28	42.0	4.3	0.8	14.1	35.3	121.77	51.14	5.21

sample	Period	days	Mass (mg)	bio-Silica (%)	OC (%)	N (%)	CaCO3 (%)	Lito (%)	mass flux (mg/(m <sup>2</sup> d))	Bio-silica flux (mg/(m <sup>2</sup> d))	OC flux (mg/(m <sup>2</sup> d))
BT98_01_02	01/01-16/1	15	138.75	16.1	15.4	2.8	46.2	0.0	18.50	2.98	2.85
BT98_03_04	16/01-1/02	16	499.28	6.8	7.6	1.4	69.7	8.3	62.41	4.24	4.73
BT98_05	01/2-15/02	14	1378.72	54.2	11.2	1.8	41.9	0.0	196.96	106.75	22.00
BT98_06	15/02-1/03	14	1170.82	65.4	5.8	0.9	5.5	17.6	167.26	109.39	9.66
BT98_07	1/03-16/03	15	1441.50	69.8	5.4	1.0	2.7	16.6	192.20	134.16	10.47
BT98_08	16/03-1/04	16	404.80	65.2	4.6	0.8	3.0	22.6	50.60	32.99	2.33
BT98_09	01/04-1/05	30	193.65	59.8	6.3	1.2	0.0	0.0	12.91	7.72	0.81
BT98_10	01/05-1/06	31	294.04	50.5	11.7	1.8	10.3	0.0	18.97	9.58	2.22
BT98_11	01/06-1/08	61	635.32	30.5	8.3	1.4	29.1	23.8	20.83	6.35	1.73
BT98_12	01/08-1/11	92	853.76	1.6	10.2	1.7	19.5	58.5	18.56	0.30	1.90
BT98_13	1/11-15/11	14	20.02	23.8	30.5	3.6	0.0	15.3	2.86	0.68	0.87
BT98_14	15/11-1/12	16	240.48	12.2	7.8	1.3	39.8	32.4	30.06	3.67	2.34
BT98_15	1/12-16/12	15	51.30	54.9	15.7	2.5	4.2	0.0	6.84	3.76	1.08

sample	Period	days	Mass (mg)	bio-Silica (%)	OC (%)	N (%)	CaCO3 (%)	Lito (%)	mass flux (mg/(m <sup>2</sup> d))	Bio-silica flux (mg/(m <sup>2</sup> d))	OC flux (mg/(m <sup>2</sup> d))
BT98_16	16/12-1/01	16	50.24	55.6	12.0	2.1	9.1	11.2	6.28	3.49	0.76
BT98_17_18	01/01-13/1	11.79	21.69	25.8	19.1	4.1	8.2	27.8	3.68	0.95	0.70
BB98_01	01/01-8/01	7	628.88	36.1	2.0	0.3	1.2	58.8	179.68	64.86	3.55
BB98_02	08/01-16/1	8	253.68	45.0	3.0	0.5	2.0	46.9	63.42	28.54	1.93
BB98_03	16/01-24/1	8	455.92	47.9	2.6	0.4	4.0	42.9	113.98	54.60	2.96
BB98_04	24/01-1/02	8	352.04	39.3	2.5	0.4	3.0	52.8	88.01	34.59	2.17
BB98_05	01/2-15/02	14	2641.66	57.5	3.7	0.6	3.9	31.2	377.38	216.99	13.98
BB98_06	15/02-1/03	14	1571.99	57.8	5.8	0.9	4.4	26.2	224.57	129.80	12.98
BB98_07	1/03-16/03	15	2140.73	65.0	4.5	0.7	18.8	7.2	285.43	185.53	12.87
BB98_08	16/03-1/04	16	1400.88	63.8	3.5	0.6	3.4	25.7	175.11	111.72	6.19
BB98_09	01/04-1/05	30	1228.95	66.2	5.0	0.9	7.4	16.4	81.93	54.24	4.11
BB98_10	01/05-1/06	31	339.61	54.5	3.0	0.6	4.1	35.3	21.91	11.94	0.67
BB98_11	01/06-1/08	61	952.82	38.4	2.6	0.5	3.5	52.9	31.24	12.00	0.82
BB98_12	01/08-1/11	92	4158.40	42.4	2.6	0.4	2.4	49.9	90.40	38.33	2.38
BB98_13	1/11-15/11	14	1387.12	1.0	6.5	1.4	0.4	85.6	198.16	1.98	12.88
BB98_14	15/11-1/12	16	464.80	39.1	2.3	0.4	1.4	54.9	58.10	22.72	1.34
BB98_15	1/12-16/12	15	693.08	57.4	3.5	0.6	2.3	33.3	92.41	53.04	3.26
BB98_16	16/12-1/01	16	864.40	54.1	3.4	0.5	1.0	38.1	108.05	58.46	3.67
BB98_17	01/01-8/01	7	680.72	57.0	4.3	0.6	0.7	33.8	194.49	110.86	8.32
BB98_18	08/01-13/1	4.79	909.07	59.6	4.0	0.7	6.2	26.2	379.57	226.22	15.10

Sample	Period	days	Mass (mg)	Bio-silica (%)	OC (%)	N (%)	CaCO3 (%)	Lito (%)	mass flux (mg/(m <sup>2</sup> d))	Bio-silica flux (mg/(m <sup>2</sup> d))	OC flux (mg/(m <sup>2</sup> d))
BT99_01	23/01-1/02	9	151.2	30.85	13.73	2.05	---	---	33.6	10.37	4.61
BT99_02	1/02-15/02	14	2552.04	21.61	5.84	0.77	---	---	364.58	78.79	21.29
BT99_03	15/02-1/03	14	5653.08	39.17	4.92	0.70	---	---	807.58	316.34	39.75
BT99_04	1/03-16/03	15	5915.52	40.5	4.82	0.73	---	---	788.74	319.4	37.98
BT99_05	16/03-1/04	16	1704.9	41.91	4.29	0.63	---	---	213.11	89.32	9.14
BT99_06	1/04-15/04	14	1567.08	53.38	2.96	0.49	---	---	223.87	119.51	6.62
BT99_07	15/04-1/05	16	888.84	55.31	4.98	0.78	---	---	111.11	61.45	5.54
BB99_01	23/01-1/02	9	1503	24.59	2.00	0.33	---	---	334	82.13	6.68
BB99_02	1/02-15/02	14	498.24	40.56	6.60	0.96	---	---	71.18	28.87	4.69
BB99_03	15/02-1/03	14	1940.4	46.56	4.62	0.63	---	---	277.2	129.06	12.80
BB99_04	1/03-16/03	15	2189.52	51.19	4.05	0.59	---	---	291.94	149.45	10.41
BB99_05	16/03-1/04	16	1927	53.37	2.45	0.38	---	---	240.88	128.56	5.90
BB99_06	1/04-15/04	14	1094.04	51.85	2.53	0.44	---	---	156.29	81.04	3.95
BB99_07	15/04-1/05	16	516.6	46.65	3.67	0.62	---	---	64.58	30.12	2.37
BB99_08	1/05-1/06	31	633.96	48.29	3.92	0.65	---	---	40.9	19.75	1.60
BB99_09	1/06-1/07	30	431.28	35.45	---	---	---	---	28.75	10.19	---
BB99_10	1/07-1/09	62	2851.92	27.55	---	---	---	---	92	25.35	---
BB99_11	1/09-1/10	30	1423.8	31.61	---	---	---	---	94.92	30	---
BB99_12	1/10-1/11	31	883.8	28.07	---	---	---	---	57.02	16.01	---
BB99_13	1/11-15/11	14	155.16	24.15	---	---	---	---	22.17	5.35	---
BB99_14	15/11-1/12	16	388.44	31.01	---	---	---	---	48.56	15.06	---
BB99_15	1/12-16/12	15	610.92	40.04	---	---	---	---	81.46	32.61	---
BB99_16	16/12-1/01	16	2097.72	43.68	---	---	---	---	262.22	114.54	---
BB99_17	1/01-8/01	7	988.56	33.19	---	---	---	---	282.45	93.74	---
BB99_18	8/01-15/01	8	1104.84	12.61	---	---	---	---	276.21	34.83	---

<b>sample</b>	<b>Period</b>	<b>days</b>	<b>Mass (mg)</b>	<b>bio-Silica (%)</b>	<b>OC (%)</b>	<b>N (%)</b>	<b>CaCO3 (%)</b>	<b>Lito (%)</b>	<b>mass flux (mg/(m<sup>2</sup>d))</b>	<b>Bio-silica flux (mg/(m<sup>2</sup>d))</b>	<b>OC flux (mg/(m<sup>2</sup>d))</b>
BB05_01	3/02 - 5/02	12	1.879.04	27.98	5.77	1.076	16.9	12.75	313.2	180.83	18.1
BB05_02	15/02-28/02	13	1.384.32	3.44	8.61	1.360	18.2	35.24	213.0	59.58	18.3
BB05_03	28/02- 10/03	10	460.12	42.52	6.04	1.422	51.1	31.97	92.0	3.16	5.6
BB05_04	10/03- 18/03	8	1.110.12	33.36	5.70	1.095	24.0	21.04	277.5	118.01	15.8
BB05_05	18/03- 31/03	13	1.464.56	14.94	7.99	1.593	35.0	14.08	225.3	75.17	18.0
BB05_06	31/03- 15/04	15	1.930.24	3.03	8.73	1.733	53.3	12.58	257.4	38.45	22.5
BB05_07	15/04 - 1/05	16	2.178.08	8.62	19.78	3.962	51.1	2.39	272.3	8.25	53.8
BB05_08	1/05 - 15/07	75	3.662.99	36.66	20.61	3.267	45.7	1.17	97.7	8.42	20.1
BB05_09	15/07 - 1/10	77	1.387.92	1.9	13.09	2.308	43.5	0.00	36.0	13.22	4.7
BB05_10	1/10 - 5/11	35	433.04	29.79	25.00	5.071	20.1	22.91	24.7	0.47	6.2
BB05_11	5/11 - 5/12	29	963.57	31.45	8.90	1.873	13.8	36.75	66.5	19.79	5.9
BB05_12	5/12 - 1/01	27	590.62	41.07	8.82	1.431	10.6	38.91	43.7	13.76	3.9
BB05_13	1/01 - 28/01	27.5	646.76	39.35	7.07	1.397	9.8	33.55	47.0	19.32	3.3

<b>sample</b>	<b>Periodo</b>	<b>days</b>	<b>Mass (mg)</b>	<b>Bio-silica (%)</b>	<b>OC (%)</b>	<b>N (%)</b>	<b>CaCO3 (%)</b>	<b>Lito (%)</b>	<b>mass flux (mg/(m<sup>2</sup>d))</b>	<b>Bio-silica flux (mg/(m<sup>2</sup>d))</b>	<b>OC flux (mg/(m<sup>2</sup>d))</b>
BB08_01	2/4 - 2/15	11	139.59	54.02	8.98	1.16	26.9	19.32	25.38	13.71	2.28
BB08_02	2/15 - 2/25	10	376.16	64.52	7.61	0.99	61.9	16.50	75.23	48.54	5.73
BB08_03	2/25 - 3/6	10	391.15	29.61	10.45	1.69	110.0	28.75	78.23	23.16	8.18
BB08_04	3/6 - 3/16	10	392.08	36.30	11.56	1.82	118.9	22.70	78.42	28.47	9.06
BB08_05	3/16 - 3/31	15	1156.80	37.64	9.38	1.65	318.2	25.76	154.24	58.06	14.47
BB08_06	3/31 - 4/15	15	1083.68	16.53	13.52	2.55	460.4	32.25	144.49	23.88	19.53
BB08_07	4/15 - 4/30	15	4569.12	6.27	18.88	3.35	2546.0	27.88	609.22	38.20	115.03
BB08_08	4/30 - 5/31	31	1.47	---	16.32	3.27	0.8	---	0.09	---	0.02
BB08_09	5/31 - 6/15	15	598.03	0.00	17.86	3.61	360.0	0.00	79.74	0.00	14.24
BB08_10	6/15 - 9/30	107	1008.37	0.00	20.66	3.41	572.9	40.33	18.85	0.00	3.89
BB08_11	9/30 - 11/1	32	26.20	---	9.41	1.41	6.2	---	1.64	---	0.15
BB08_12	11/1 - 1/15	14	0.00	---	---	---	---	---	---	---	---
BB08_13	11/15 -12/1	16	2.68	---	12.10	2.12	0.8	---	0.34	---	0.04
BB08_14	12/1 - 2/16	15	0.00	---	---	---	---	---	---	---	---
BB08_15	12/16 - 1/1	16	1.05	---	6.70	1.16	0.2	---	0.13	---	0.01
BB08_16	1/1 - 1/8	7	7.81	---	11.13	1.61	4.5	---	2.23	---	0.25
BB08_17	1/8 - 1/16	8	17.22	---	9.65	1.4	8.0	---	4.31	---	0.42
BB08_18	1/16 - 1/24	8	2.05	---	7.12	0.75	0.2	---	0.51	---	0.04
BB08_19	1/24 - 2/1	8	805.81	0.97	12.94	1.21	161.9	1.31	201.45	1.95	26.08
BB08_20	2/1 - 3/1	28	690.24	2.19	13.16	1.12	36.9	13.96	49.30	1.08	6.49
BB08_21	3/1 - 1/1/10	306	1.50	---	18.97	---	0.0	---	0.01	0.00	0.00

## Sea ice concentration (%)

	MA		MB				
	2005	2008	1996	1998	1999	2005	2008
1-Jan	20.4	31.2	0	32.4	0	0	0
2-Jan	23.2	19.6	0	30	0	0	0
3-Jan	20.8	18.4	0	30.8	0	0	0
4-Jan	26.8	18.8	0	32.8	0	0	0
5-Jan	24.8	18	0	32.4	0	0	0
6-Jan	24	17.2	0	31.2	0	0	0
7-Jan	22	13.6	0	29.2	0	0	0
8-Jan	18.4	15.2	0	27.2	0	0	0
9-Jan	13.6	13.2	0	22.8	0	0	0
10-Jan	17.2	0	0	20.4	0	0	0
11-Jan	10.4	0	0	18	0	0	0
12-Jan	9.2	0	0	18	0	0	0
13-Jan	15.6	0	0	17.6	0	0	0
14-Jan	17.2	0	0	15.6	0	0	0
15-Jan	20	0	0	10.4	0	0	0
16-Jan	15.6	0	0	0	0	0	0
17-Jan	14	0	0	4	0	0	0
18-Jan	12.4	0	0	0	0	0	0
19-Jan	9.2	0	0	9.2	0	0	0
20-Jan	14	0	0	10.4	0	0	0
21-Jan	13.2	0	0	0	0	0	0
22-Jan	9.2	0	0	0	0	0	0
23-Jan	20.8	0	0	0	0	0	0
24-Jan	14.8	0	0	1.6	0	0	0
25-Jan	10.4	0	0	0	0	0	0
26-Jan	12	0	0	0	0	0	0
27-Jan	7.2	0	0	0	0	0	0
28-Jan	7.6	0	0	0	0	0	0
29-Jan	6.4	0	0	0	0	0	0
30-Jan	6	0	0	0	0	0	0
31-Jan	0.8	0	0	0	0	0	0
1-Feb	8.8	0	0	0	0	0	0
2-Feb	8	0	0	0	0	0	0
3-Feb	12.8	0	0	0	0	0	0
4-Feb	5.6	0	0	0	0	0	0
5-Feb	10.4	0	0	0	0	0	0
6-Feb	5.6	0	0	0	0	0	0
7-Feb	8.4	0	0	0	0	0	0
8-Feb	5.6	0	0	0	0	0	0

	MA		MB				
	2005	2008	1996	1998	1999	2005	2008
9-Feb	9.2	0	0	0	0	0	0
10-Feb	8	0	0	0	0	0	0
11-Feb	6.4	0	0	0	0	0	0
12-Feb	6	0	0	0	0	0	0
13-Feb	5.6	0	0	0	0	0	0
14-Feb	6.8	0	0	0	0	0	0
15-Feb	8.4	0	0	0	0	0	0
16-Feb	9.6	0	0	0	0	0	0
17-Feb	7.6	0	0	0	0	0	0
18-Feb	16.8	0	0	0	0	0	0
19-Feb	10	0	0	0	0	0	0
20-Feb	16.4	0	0	0	0	0	0
21-Feb	19.6	2.8	0	0	0	0	0
22-Feb	11.2	10.4	0	0	0	0	0
23-Feb	15.6	6.8	0	0	0	0	0
24-Feb	13.2	7.6	0	0	0	0	0
25-Feb	16.4	7.2	0	0	0	0	0
26-Feb	15.6	8	0	0	0	0	0
27-Feb	18	24.4	0	0	0	0	0
28-Feb	14.4	26	0	0	0	0	0
1-Mar	19.6	26.4	0	0	0	0	0
2-Mar	21.6	43.2	0	0	0	0	0
3-Mar	28	52	0	0	0	0	8.4
4-Mar	22.4	46.4	0	0	0	0	8.4
5-Mar	22.8	42	0	0	0	0	24.4
6-Mar	24.4	64	0	16.4	0	0	28.8
7-Mar	31.2	62.8	0	28.8	0	0	30
8-Mar	42.4	68	0	36.4	0	0	40.8
9-Mar	44	67.6	0	48.8	0	0	50
10-Mar	48.4	66	0	56	0	0	47.2
11-Mar	52.8	65.6	0	63.2	0	0	60.4
12-Mar	52.8	78.4	0	70.4	0	0	66
13-Mar	57.2	81.2	0	66.4	0	0	69.6
14-Mar	62.4	83.6	0	65.2	0	0	73.6
15-Mar	80	85.2	0	62.4	0	0	75.6
16-Mar	80.8	84.4	0	67.6	0	0	76.8
17-Mar	78.4	83.6	0	68.8	0	0	74.8
18-Mar	84.8	89.6	0	71.2	0	0	78.4
19-Mar	80	90	0	73.6	0	0	80.8
20-Mar	78.4	87.2	0	74.4	0	0	81.6
21-Mar	74.4	84.8	0	84.8	26.8	0	82.4
22-Mar	66	82.4	5.6	85.2	44.4	0	83.2
23-Mar	69.6	80	19.2	88	50	0	83.6

	MA		MB				
	2005	2008	1996	1998	1999	2005	2008
24-Mar	71.6	77.2	23.2	90	64.8	12.8	84.4
25-Mar	73.2	74.8	27.6	90.4	80	40	84.8
26-Mar	73.2	72.4	27.2	92	78.4	56.8	85.6
27-Mar	68.4	69.6	49.2	94.4	80.8	62.8	86.4
28-Mar	69.6	66.8	58.4	94.8	78.8	64.8	85.2
29-Mar	68.4	68.4	62.4	94.8	79.6	65.6	84.8
30-Mar	75.6	62.4	63.2	84.8	85.2	72.4	82.4
31-Mar	82.4	64.4	62.8	90.8	87.6	76.8	87.2
1-Apr	85.6	70.4	71.6	74.8	88.4	74	92.4
2-Apr	82	72.4	75.6	72.8	85.6	74	93.6
3-Apr	84.8	72	84.8	78.4	85.2	73.2	93.2
4-Apr	84	72.4	84.8	82	83.6	76.4	92.8
5-Apr	78	72	86	82.8	81.6	76.8	91.6
6-Apr	79.6	71.2	91.2	87.2	80.4	80	89.6
7-Apr	76.4	75.2	92	90.8	86.4	84	90
8-Apr	78.8	73.6	88.8	92.4	88.8	90.8	91.6
9-Apr	84	71.2	92	92.4	90.8	90.8	91.6
10-Apr	86.4	72	91.6	92.4	90.4	89.2	89.2
11-Apr	89.2	70	89.2	93.6	85.6	93.2	94
12-Apr	85.6	70	86.8	93.2	83.2	97.2	90
13-Apr	87.6	71.2	81.2	92.8	86	99.6	92
14-Apr	87.2	74	88.8	92.8	87.6	98	90.4
15-Apr	88	74	93.2	93.6	84.8	98.8	90
16-Apr	88.8	73.6	87.6	94	84.4	100	91.6
17-Apr	88.8	76.4	84.4	94.4	94	100	91.6
18-Apr	91.2	80	87.2	93.2	90.8	100	94.4
19-Apr	94	78	86.8	94.4	96	100	93.2
20-Apr	95.2	84.8	87.2	95.2	91.6	98.4	94.8
21-Apr	97.2	84	85.2	96	94.4	95.6	96
22-Apr	95.2	84	86	98.8	89.2	95.6	94.8
23-Apr	84.4	85.2	91.2	98	96	93.6	94
24-Apr	86	81.6	92	96	96	90.8	91.6
25-Apr	85.2	82.8	91.2	94.4	96.4	86.4	86.8
26-Apr	84.4	76.8	88	93.2	98	80.8	78.4
27-Apr	84.4	66.8	85.6	88.4	92.8	81.6	84
28-Apr	82.4	73.6	85.2	88.8	88.4	81.2	88
29-Apr	82.8	76	85.6	91.6	90.4	75.2	88
30-Apr	86	74.4	84.8	96.4	91.2	77.6	88.8
1-May	88.4	81.6	86	96.4	93.6	83.6	89.2
2-May	85.2	86.8	89.6	93.2	91.2	84	93.6
3-May	83.6	85.2	91.6	95.6	90.8	88.4	92
4-May	82.4	83.2	94	92.8	94.4	84.8	90.4
5-May	84.8	75.2	94.8	89.6	94.8	86.8	85.6



	MA		MB				
	2005	2008	1996	1998	1999	2005	2008
6-May	82.4	79.6	94	89.2	96.4	90.8	86.4
7-May	78	82	89.2	89.6	96	97.2	86.4
8-May	77.6	85.2	87.2	87.2	96.8	95.6	88.4
9-May	73.2	85.2	85.6	84	94	94	88.8
10-May	69.6	85.2	83.2	89.6	94	94.4	91.2
11-May	72.4	87.2	93.2	94	94	92.8	92
12-May	72.8	88.8	93.2	93.2	94.8	92.8	93.2
13-May	74.8	89.6	91.6	89.6	94.4	90.4	94.8
14-May	75.6	90	88	91.2	94.8	89.2	92.8
15-May	76	83.6	85.6	89.2	96.4	88.4	95.2
16-May	81.6	87.2	84.8	88	96.4	89.6	95.2
17-May	73.6	86	88.8	85.2	96	91.6	96.4
18-May	70.4	89.2	90.8	85.6	96	89.6	96.4
19-May	78.4	90.4	93.6	92	96.8	91.2	97.6
20-May	81.2	92	95.6	97.2	97.2	92.4	94.4
21-May	85.2	92.4	95.2	99.2	96.8	92.8	95.6
22-May	83.6	94.4	95.2	97.6	96.4	92	96
23-May	82.4	96.4	95.2	98.8	93.6	90.8	95.6
24-May	82.8	94.8	94.4	96.8	94.4	83.6	93.6
25-May	72.8	94.4	98	96.8	94	83.6	92.8
26-May	74.8	90.4	91.6	95.6	92	81.2	94
27-May	79.2	91.6	91.6	94	92	74	93.6
28-May	80	93.2	90.4	94	84.8	95.6	94.8
29-May	78.4	93.2	90.8	95.2	85.6	84.8	96
30-May	76	91.2	91.2	93.2	86.8	88.4	95.6
31-May	82.4	92	94.4	90	87.2	94.4	94
1-Jun	82.8	90	98	93.2	86.4	88.8	92.4
2-Jun	77.6	84.8	94	94	89.6	89.6	92.4
3-Jun	81.6	83.6	89.6	91.2	97.6	85.2	94.4
4-Jun	83.6	83.6	98	88.4	92.8	89.6	92.8
5-Jun	84.4	75.2	96.4	87.6	82	89.6	92.8
6-Jun	88.4	72.8	94.8	82.4	96	89.2	90.4
7-Jun	90.4	76.8	92	91.6	93.6	91.6	90.8
8-Jun	86.8	72.8	92.4	92.8	90	89.6	93.2
9-Jun	88.8	70.8	93.2	92.8	90.4	88.8	92.8
10-Jun	90.4	82.8	94	92.8	88.8	90.8	94.4
11-Jun	92.4	82.8	93.6	91.6	84.8	90.8	91.2
12-Jun	89.2	81.2	94	94.4	83.6	90.8	93.6
13-Jun	87.6	85.2	93.2	94	85.2	90	94.4
14-Jun	86	83.6	92.8	92.4	74.4	90.4	94.4
15-Jun	86.8	88.4	96.4	91.6	73.2	90.4	93.2
16-Jun	82.8	86.4	97.2	90.4	74.4	91.6	90.8
17-Jun	86.4	85.2	95.6	97.2	83.6	93.2	89.2

	MA		MB				
	2005	2008	1996	1998	1999	2005	2008
18-Jun	86	88	92.8	95.2	90.4	95.2	88.8
19-Jun	86.4	84.4	92.4	95.2	91.6	96.8	96
20-Jun	85.6	92	96	94	90.4	94.8	97.6
21-Jun	88.8	92.4	97.6	95.6	91.6	95.2	97.2
22-Jun	72.4	93.2	92.4	96	94.4	88.4	98
23-Jun	74	94	86.4	92	96.8	88.4	98.8
24-Jun	65.2	94.4	86.8	88.4	98	94	95.6
25-Jun	70.8	93.6	87.2	92.8	98	90.4	96.4
26-Jun	77.6	86	81.6	92.8	98	88	98
27-Jun	78.4	85.2	88	90.4	98	86	95.6
28-Jun	80.8	88	85.6	88.4	93.2	86.4	88
29-Jun	65.2	88	82.8	84	88.8	80.4	86.8
30-Jun	56.8	90.8	88	80.8	89.2	89.2	89.6
1-Jul	63.2	92	88	80.8	92.4	88	90.4
2-Jul	71.2	94	89.2	84	87.6	92.4	91.6
3-Jul	70.8	96	85.2	82.8	86.4	92.8	92.8
4-Jul	76	97.2	83.6	75.6	88	90	89.2
5-Jul	73.2	98	86	78	85.6	83.6	92.4
6-Jul	79.6	97.2	85.6	82.8	86	80	94.4
7-Jul	84.4	97.6	89.2	94.4	84.4	82	92.8
8-Jul	85.6	98	90.8	86.8	88.4	83.6	92.8
9-Jul	87.2	97.6	92	84	83.6	81.6	91.6
10-Jul	87.2	94	90	85.2	84.8	82.4	92.4
11-Jul	87.2	95.2	91.6	94.4	86.4	79.6	91.2
12-Jul	92	97.6	88.4	95.2	79.6	79.6	92.4
13-Jul	90.4	96.8	83.2	97.2	83.2	82.8	92.8
14-Jul	88.4	94.8	85.6	91.6	90	82.8	91.2
15-Jul	90.8	95.2	84.4	90	97.6	83.2	92
16-Jul	90	89.6	84.4	85.2	97.2	87.2	92.8
17-Jul	90.8	91.2	87.2	84	93.6	86	97.2
18-Jul	92	92	86.4	84.8	87.6	85.2	98.8
19-Jul	94	92	90	88.4	78.8	90.8	99.2
20-Jul	88.4	91.2	93.2	85.2	70	95.6	100
21-Jul	84	94	94	84.8	86.4	96.4	100
22-Jul	74.4	96.8	87.2	89.2	88.8	91.2	97.6
23-Jul	74.4	96.8	87.2	84.4	90	90	96.8
24-Jul	77.2	98.8	85.2	83.6	92	88	96.4
25-Jul	84.4	100	90	85.2	88.4	90	96
26-Jul	81.6	97.6	91.6	88	76.8	94.4	95.6
27-Jul	84.4	98	93.6	90.8	77.6	90.8	96.4
28-Jul	82.4	98	93.6	92.8	74.4	91.2	97.2
29-Jul	88	92	95.6	95.2	77.6	88.8	98
30-Jul	88.4	88.8	95.6	96.8	95.2	85.2	96.4

	MA		MB				
	2005	2008	1996	1998	1999	2005	2008
31-Jul	88.8	88.4	94.8	93.6	92.8	84.8	94.4
1-Aug	86.8	89.6	84.8	94.8	92	86.8	93.2
2-Aug	88.4	90.4	73.6	97.2	92.8	86.4	94.8
3-Aug	82	91.6	76	97.6	91.6	91.2	94.8
4-Aug	84.4	90.8	79.2	97.6	89.6	86	95.6
5-Aug	86.8	94.4	80	94	89.2	83.6	97.6
6-Aug	89.6	98	80.4	92	86.4	85.2	99.2
7-Aug	91.2	98	89.2	88.8	88.8	84.8	99.6
8-Aug	94.8	98.8	92.4	94	88.8	94.8	100
9-Aug	93.2	99.6	93.2	92.4	91.2	88	100
10-Aug	93.6	99.2	95.2	90	88	91.6	100
11-Aug	92.4	100	90.8	86.8	90.4	91.2	100
12-Aug	88.4	100	90.4	86.4	93.2	90.4	100
13-Aug	90.8	100	91.6	83.2	94.8	90.4	100
14-Aug	91.6	99.6	90.4	80	97.6	92.4	100
15-Aug	89.2	99.6	88.4	83.6	97.2	94.8	100
16-Aug	87.6	96	91.6	86.8	100	91.2	96
17-Aug	84	96.4	92	88	98	81.6	98.4
18-Aug	69.2	96.8	90.4	88.4	98.4	78	95.2
19-Aug	74	97.2	95.6	86	98.8	81.2	95.6
20-Aug	72.4	98.8	92.4	85.2	94.8	83.2	98.4
21-Aug	80.4	100	92.4	85.6	94	88	99.2
22-Aug	88.8	98	90.4	82.4	96	96	96.8
23-Aug	85.2	99.6	88	83.2	96.4	95.2	96.8
24-Aug	66	100	85.2	85.2	97.2	98	96.8
25-Aug	67.6	100	81.6	83.2	96.8	94.4	96.4
26-Aug	79.6	100	82	84.4	97.2	90	96.4
27-Aug	84	100	85.2	79.6	96.4	89.2	96.4
28-Aug	82	100	87.2	67.2	98.4	92.4	96
29-Aug	85.6	100	91.2	83.6	98.8	94.8	98
30-Aug	86.4	100	94.8	74.4	97.6	95.6	98.8
31-Aug	88.4	100	84.8	80.4	98.8	94	99.6
1-Sep	84	100	86	82.4	98.8	94	100
2-Sep	87.2	100	97.6	91.6	98	92.4	100
3-Sep	86	100	96.4	93.2	96.8	91.2	100
4-Sep	82.8	100	96.4	94.4	95.6	93.6	100
5-Sep	86	100	93.2	94.4	96	94.8	100
6-Sep	84.8	100	92.8	95.2	88.8	94	100
7-Sep	86	96	91.2	86.8	88	94	100
8-Sep	86	96.4	89.2	80	88.8	93.6	100
9-Sep	88.8	96.8	86.4	79.2	86.4	94.8	100
10-Sep	89.6	97.2	86.4	82.4	87.2	95.2	100
11-Sep	90.4	96.8	88.4	88.4	88.4	96	100

	MA		MB				
	2005	2008	1996	1998	1999	2005	2008
12-Sep	89.6	98	88.4	79.2	90.4	96.8	100
13-Sep	90.8	94.8	89.2	77.6	92	99.6	100
14-Sep	82.8	96.8	97.6	86.8	92.4	98	100
15-Sep	84.8	97.6	97.6	86.8	93.6	96.4	100
16-Sep	77.6	96.8	96	88.4	92.4	98	100
17-Sep	74.4	96.8	96.4	92.4	91.2	91.6	98
18-Sep	76	98.8	94	90.4	91.2	89.2	100
19-Sep	74.8	94.8	92	86.4	95.6	88	100
20-Sep	75.6	86.4	92.4	89.2	95.2	88.4	96.8
21-Sep	75.6	85.2	92.4	88	94.8	90	94.8
22-Sep	83.2	87.2	95.2	86.8	93.2	92.8	95.6
23-Sep	83.2	82.4	97.2	88.4	90	94.8	94
24-Sep	83.2	77.2	97.6	90.4	90.8	96	93.6
25-Sep	84.4	74.4	89.6	91.2	91.6	96	92.8
26-Sep	84.8	79.6	89.2	92.4	92.8	94.4	91.6
27-Sep	85.2	77.2	93.6	92.8	96.4	93.6	92
28-Sep	85.2	78	93.2	92.8	100	92.8	89.6
29-Sep	86.8	78.8	94	86	100	90.4	90.4
30-Sep	86	82	93.6	87.6	98.4	88.8	91.6
1-Oct	83.2	84.8	90	89.2	96.4	90	92.8
2-Oct	78.8	86	88.8	88.4	95.2	90.4	94
3-Oct	80.8	90	88.8	90	94.8	88.8	93.6
4-Oct	82.4	94	90.4	91.2	96	90.8	90.4
5-Oct	81.2	86.4	86.8	91.6	98.4	94	85.2
6-Oct	88	85.6	82.8	87.6	95.2	94.8	76.4
7-Oct	87.2	84.4	73.2	90.4	98.4	92	95.6
8-Oct	86.8	88.4	72.8	91.2	98.4	93.6	91.2
9-Oct	80.8	87.2	71.2	87.6	99.2	93.6	92.4
10-Oct	84	89.6	74.4	87.6	98.4	96.4	93.6
11-Oct	78.4	89.2	76	91.2	98.4	93.6	92.8
12-Oct	75.6	88	74.8	64.8	98.8	91.6	91.6
13-Oct	65.6	86.8	86	86.8	98	90	91.6
14-Oct	68.4	86.4	86.8	89.6	92.4	92.8	92.4
15-Oct	70	88.8	92	88.8	87.6	91.6	92
16-Oct	71.6	88.8	91.2	91.6	87.6	91.2	90.4
17-Oct	80.4	83.2	86.4	89.6	88	90.8	92
18-Oct	81.2	86.8	79.2	92	88.4	91.6	90
19-Oct	80.8	87.6	82.4	95.2	90	94.8	90.8
20-Oct	84.4	90.4	90.4	94.4	88.8	93.2	92
21-Oct	65.6	91.6	90.4	96.8	86.4	86.8	94
22-Oct	62.4	90.8	92.8	91.6	86.4	77.6	92.8
23-Oct	63.2	90	91.2	89.2	92.4	81.6	90
24-Oct	62.4	90.8	92.4	87.6	91.2	74	90

	MA		MB				
	2005	2008	1996	1998	1999	2005	2008
25-Oct	61.6	88.8	92.8	88.8	90.8	66.4	90.4
26-Oct	62	85.2	93.6	86.8	91.2	63.6	90.8
27-Oct	58.4	88	90	87.6	91.2	59.2	91.6
28-Oct	64	90.4	90.8	85.6	94.4	58.4	92
29-Oct	62.4	88.8	91.2	85.6	90.8	58.4	91.2
30-Oct	64	88	90.4	86	90.8	57.2	92.4
31-Oct	60.4	90	93.2	84	94	56.4	94
1-Nov	57.6	91.6	94.4	82.4	86	73.2	95.6
2-Nov	55.6	91.6	96	80.8	77.6	78.8	91.2
3-Nov	56	92.4	94.8	78	80.4	90.8	89.6
4-Nov	60.8	94.4	98.8	73.2	79.2	88	88.4
5-Nov	60	90.8	91.2	66.8	74.8	85.2	88
6-Nov	58	89.6	89.2	66.8	71.6	76.4	86.4
7-Nov	56.4	90	94	63.6	72.4	79.2	85.6
8-Nov	55.2	86.8	91.2	66.4	67.2	85.2	86
9-Nov	56.8	86.4	88	79.6	70.8	89.2	85.6
10-Nov	58.8	84.8	83.6	78	73.6	87.6	85.2
11-Nov	50	83.6	84.8	70	75.2	86.8	84.4
12-Nov	66.4	83.6	86.8	61.6	65.2	85.6	86.4
13-Nov	64.4	80.8	80	71.6	65.6	85.2	88
14-Nov	69.2	82.4	84.8	72.4	64.8	87.6	86.8
15-Nov	66.4	81.6	80.8	68.8	66	88	86.4
16-Nov	63.6	82.4	81.2	74	72.4	88.4	86.8
17-Nov	58	82.8	82	70.4	65.6	86.4	85.2
18-Nov	60.4	86	76	67.2	66	86.8	83.6
19-Nov	64.8	87.6	74.8	65.6	63.6	86.8	82.4
20-Nov	60	89.2	76.8	66	64.8	86	82
21-Nov	57.6	86.4	75.2	64.8	64.4	81.6	80.4
22-Nov	54	83.2	76	61.6	66	78.8	81.6
23-Nov	59.2	84	78.4	60	64.4	75.2	82
24-Nov	62.4	80.8	80.4	60.4	59.6	74.4	83.6
25-Nov	58.8	80.8	78.4	58.4	57.2	68.4	83.2
26-Nov	63.2	76	65.2	58.8	41.6	63.2	82
27-Nov	63.6	74.8	70.4	57.6	39.2	61.2	80.8
28-Nov	60.4	72	62.8	71.6	26.8	59.2	83.2
29-Nov	61.2	59.2	58.8	70.4	12	62	80.4
30-Nov	55.2	49.6	40.8	66	0	55.2	79.2
1-Dec	51.6	49.2	28.4	65.2	0	26.8	75.2
2-Dec	37.2	50.4	14.4	60.4	0	12.4	76.8
3-Dec	30.8	48	0	56.8	0	0	78.8
4-Dec	25.2	50.4	0	66.8	0	0	80.4
5-Dec	24.4	53.6	0	61.2	0	0	79.2
6-Dec	31.2	51.2	0	65.6	0	0	74.8

	MA		MB				
	2005	2008	1996	1998	1999	2005	2008
7-Dec	28.8	52	0	69.6	0	0	71.6
8-Dec	28.4	50.8	0	60.8	0	0	66.4
9-Dec	26.8	54.4	0	58.8	0	0	68
10-Dec	23.6	52	0	64	0	0	71.2
11-Dec	20	53.6	0	63.6	0	0	68.4
12-Dec	25.6	52.8	0	58.8	0	0	71.2
13-Dec	20.4	53.2	0	62	0	0	71.2
14-Dec	14.4	52	0	59.2	0	0	66.4
15-Dec	17.6	52.4	0	39.6	0	0	60.4
16-Dec	11.2	51.2	0	23.6	0	0	53.6
17-Dec	22.4	50	0	7.2	0	0	37.2
18-Dec	20.4	53.2	0	3.6	0	0	37.2
19-Dec	14	55.6	0	14.4	0	0	40
20-Dec	12.4	53.6	0	10	0	0	45.6
21-Dec	0	53.6	0	0	0	0	37.2
22-Dec	9.2	54	0	0	0	0	28
23-Dec	9.2	51.6	0	0	0	0	23.6
24-Dec	13.6	53.2	0	0	0	0	14.8
25-Dec	11.6	51.6	0	0	0	0	3.6
26-Dec	13.2	50.8	0	0	0	0	0
27-Dec	10.4	51.6	0	0	0	0	0
28-Dec	12.8	45.6	0	0	0	0	0
29-Dec	9.2	45.6	0	0	0	0	0
30-Dec	11.2	49.2	0	0	0	0	0
31-Dec	6.4	49.2	0	0	0	0	0

## Chlorophyll a concentrations (mg/m<sup>3</sup>)

	MA		MB	
	2004/05	2007/08	2004/05	2007/08
8-Nov	0.144			
16-Nov				
24-Nov	0.395		4.509	
2-Dec	0.513		1.308	
10-Dec	0.892	0.438	1.029	0.227
18-Dec	1.395	0.759	3.801	0.367
26-Dec	0.751		4.305	0.497
1-Jan	0.763	4.767	3.724	0.339
9-Jan	0.25	1.987		0.461
17-Jan	0.216	0.536	0.824	0.332
25-Jan	0.231	0.301	0.51	0.316
2-Feb	0.255			0.552
10-Feb	0.213	0.517	0.325	0.359
18-Feb	0.18	0.497		0.648
26-Feb	0.169			0.501

	MB			
	1996/97	1998/99	2004/05	2007/08
Dec		1.357	2.749	0.363
Jan		1.104	2.17	
Feb	0.778	0.703	0.274	
Mar	0.542			

## Picking tables

Number of organisms per sample  
(M = many, S = some, F = few)

MA 2005 Top	Samples										
	1	2	5	7	9	10	11	13	14	15	17
Amphipoda		1	27	2		1			3		
Copepoda			14								
Euphausiacea (Krill)		1	8								
Limacina helicina		3	140								
Polychaeta			100						7	13	
Larvae			2						2		
Ostracoda											
Foraminifera											
Radiolaria											
Fecal Pellets	M	M			F						F
Moults										3	3
Mucilaginous clusters	F	M									
Algae			M								
Ophiuroidea			31						1		



MA 2005 Bottom	Samples												
	1	2	4	7	9	10	12	14	15	16	17	18	20
Amphipoda				21	7	50							2
Appendicularia													
Copepoda				7		3							1
Euphausiacea (Krill)				2		2							
Limacina helicina													
Polychaeta				162	13	69					1		1
Larvae				15	8	67							
Ostracoda						9							
Ctenophori				5	2								
Foraminifera													
Radiolaria													
Fecal Pellets	F	F											
Moult													
Mucilaginous clusters				M		S							
Algae													
Ophiuroidea				68	2	9							

MA 2008 Top	Samples											
	1	2	3	4	5	6	7	8 - 9	10	11	12	13
amount (ml)	3	2	0.25	0.25	0.8	0.5	2	1.5	1	2	2	3
Plankton	13	2	19	29	20	7		4	5	2	8	
Foraminifera		1	2	1	1	4	1	5			2	1
Limacina helicina	3	6	48	17	18	6	4	7				2
Copepoda	3						5	4	1	1		1
Dinoflagellates	20	7	11	17	7	3	2	1	0	5	14	39
Cystis	3	0	2	5	0	3	0	0	0	0	10	2

MB 1999 Top	Samples						
	1	2	3	4	5	6	7
Amphipoda	32	46	19	12	10	6	
Appendicularia	3	65	15	47	127	7	4
Copepoda	29	49	39	55	24	39	70
Euphausiacea (Krill)							
Limacina helicina	235	2475	383	303	105	197	1468
Naupilus	2	5	2				
Polychaeta	1	17	10	30	5	2	8
Larvae	1	2	1				
Ostracoda		1	4			3	7
Foraminiferi	M	M	F	F	F		F
Radiolari							
Fecal Pellets	S	M	M	M	M	F	F
Moults							
Mucilaginous clusters	S	S		S	S	S	
Algae							
Ophiuroidea							

MB 1999 Bottom	Samples																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Amphipoda																1		
Appendicularia		1																
Copepoda	3	8	16	7	13	9	18	37	36	70	12	13	2	2	2			
Euphausiacea (Krill)																		
Limacina helicina	4	3	54	239	238	250	109	120	96	92		1		1				
Polychaeta	5	1	4	6	6		1	2	1	128	9	1	1		1	2		1
Larvae																		
Ostracoda		1	3	2	6		2	1	3	10	9	14	8	19	10	5	2	4
Foraminifera	F		F	F		F	F	F	F				F	F		F	F	
Radiolari																		
Fecal Pellets	F	F	F	M	F	F	F		F	F	F	S	S	S	S	S	F	S
Moult																		
Mucilaginous clusters	M	M	S	S	M	M	M	M	M	M	M	S	S		M	S	M	M
Algae																		
Ophiuroidea																		

MB 2005 Bottom	Samples												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Amphipoda	141	126	114	87	98	105	49	66	61	53	28	7	13
Appendicularia													
Copepoda	9	10	27	17	19	22	20	13	34	5	8	2	11
Euphausiacea (Krill)													
Hydromeduse		3	6	10	23	28	23	89	56	12	2	5	
Limacina helicina	21	1473	3834	1353	4775	4743	5704	8680	2889				
Polychaeta	18	36	30	26	84	100	97	138	90	25	8	12	9
Larvae													
Ostracoda	2	3		7	12		4	7	17			2	1
Foraminifera		22	25	11	19	75	28	86	127				
Radiolari													
Fecal Pellets													
Moult	7	13	2	7	4	3	13	10	10	5	17	7	4
Mucilaginous clusters													
Algae													
Ophiuroidea		1	2		1				2	9	18	6	9

MB 2008 Bottom	Samples												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Amphipoda	4	3	1	2	12	6	5		15				1
Appendicularia									4				
Copepoda										10			
Euphausiacea (Krill)				2						1			
Limacina helicina	7	56	1000	200	3392	5691	4717		11408	8000			
Polychaeta	6		13	3	12	23	14		18	1			
Larvae					2				7	7			
Ostracoda			1										
Foraminifera					13		50						
Radiolari													
Fecal Pellets			M										
Moults	2												
Mucilaginous clusters			M	S		M	S						
Algae							F		S				
Ophiuroidea	3	1			9	1			3	13	1		2